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LXVIII. *Atomic Scattering Factors of Nickel, Copper, and Zinc.* By G. W. BRINDLEY, M.Sc., Ph.D., and F. W. SPIERS, Ph.D., *Physics Laboratories, University of Leeds* *.

1. *Introduction.*

AS a preliminary to a series of X-ray experiments on metals and alloys, we have found it necessary to determine accurately the atomic scattering factors of nickel, copper, and zinc for $\text{CuK}\alpha$ radiation ($\lambda = 1.539 \text{ \AA.U.}$). Measurements for copper have previously been made by Armstrong ⁽¹⁾, Wyckoff ⁽²⁾, and Rusterholz ⁽³⁾; our results are in substantial agreement with the last two investigators. For nickel, the only previous measurements appear to have been made by Wyckoff ⁽²⁾; our results for this metal are appreciably different from Wyckoff's. No previous measurements appear to have been made for zinc.

The atomic scattering factor \dagger , f , is a function of $(\sin \theta)/\lambda$ and for a given reflexion is independent of λ ,

* Communicated by Prof. R. Whiddington, F.R.S.

\dagger The atomic scattering factor is defined as the amplitude scattered by an atom in a direction 2θ with respect to the incident direction (θ is the Bragg angle of reflexion), measured in terms of the amplitude scattered by a single free electron.

the wave-length of the radiation. This is only correct if dispersion effects can be neglected; these are important when λ is comparable with λ_k , the wave-length corresponding to an absorption edge of the scattering atom. In the present experiments, $\lambda/\lambda_k = 1.037, 1.117$, and 1.202 for Ni, Cu, and Zn respectively. In all three cases dispersion will have an important effect on the scattering factors, and it is therefore very desirable that experimental results for this frequently used wave-length should be available.

A powder method has been used in this work, and special care has been taken to satisfy experimentally the conditions assumed in the theory of X-ray reflexion from fine powders. Absolute values have been obtained by comparing reflexions from the metal investigated with reflexions from finely powdered KCl. The atomic scattering factor of KCl has been measured absolutely by James and Brindley⁽⁴⁾ for $\text{MoK}\alpha$ radiation. To obtain the corresponding values for $\text{CuK}\alpha$ radiation, a small dispersion correction of the order of 3 per cent. is required which has been made on the basis of Hönl's⁽⁵⁾ method. Any subsequent recalculation of this correction by more exact methods is unlikely to affect our scattering factors for Ni, Cu, and Zn by more than 1 or 2 per cent.

2. Preparation of the Powders.

Special care has been taken to obtain powders having a sufficiently small particle size. Usually the particles of a powder do not consist of single crystals, but of a cluster of smaller crystals which cannot easily be separated. The importance of having sufficiently small particles has been discussed by Schäfer⁽⁶⁾, Brentano⁽⁷⁾, and by the present writers⁽⁸⁾. In order to use the mixture method of standardizing intensities from powders, it is essential that a large fraction of the radiation incident on each particle shall be transmitted, for it is only when this condition is satisfied that a sufficient number of particles will reflect radiation. By using two largely independent methods of standardizing the intensities, we have obtained a direct experimental check that our powders have consisted of sufficiently small particles.

It is important that the individual crystals shall be small in order to reduce to a minimum effects due to extinction; this will be discussed further in section 5.

The elimination of extinction effects requires a much smaller crystal size than is usually necessary to obtain satisfactory powder mixtures, but in some cases it happens that small crystals occur grouped together in relatively large particles.

Copper.—This was prepared by the addition of finely powdered zinc to copper sulphate solution; the precipitate was carefully washed and then dried in a vacuum. The finest particles were selected by means of a sieve having a 350 mesh to the linear inch; their size was of the order of 5×10^{-4} cm. Microscopic examination showed that the particles consisted of clusters of much smaller crystals.

Nickel.—This was obtained by the reduction of nickel formate heated to 500° C. in a stream of hydrogen. The powder was sieved as above, and the particle size was of the order of 3×10^{-4} cm.

Zinc.—Very fine zinc powder was prepared by the sublimation of pure zinc filings heated *in vacuo* to prevent oxidation. The zinc vapour condensed on the walls of the glass tube where it emerged from the furnace, and, by slowly withdrawing it, a thin deposit of zinc powder was obtained.

KCl.—Sufficiently fine particles could not be obtained by prolonged mechanical grinding, and the possibility that such grinding might distort the crystals made this method not very suitable. Very fine crystals were obtained by dissolving metallic potassium in alcohol and passing chlorine or HCl gas through the solution, or adding concentrated HCl solution directly. The particle size measured under the microscope was of the order of 5×10^{-4} cm., but the individual crystals were much smaller.

3. *Experimental Method.*

The method adopted for measuring reflected X-ray intensities photographically has already been described by ourselves ⁽⁸⁾ and by Brentano ⁽⁷⁾ ⁽⁹⁾, and needs only brief mention here. A fine beam of X-rays, having a spread of about 2° , is reflected from a plane stationary block of powder mounted at the centre of a cylindrical camera, and the reflexions are recorded on a photographic film wrapped round the outside. The powder holder

is a block of mild steel machined so that its face is accurately plane and lies exactly on the axis of the camera when mounted in position. It has two parallel cavities, one just below the other, about 2.5 cm. long, 1 cm. wide, and 1.5 mm. deep.

For determining relative intensities from one powder, the holder is set with its face at a suitable angle α to the X-ray beam so that a certain group of reflexions is most satisfactorily recorded. The variation of focussing along the film, and of the absorption in the powder for different reflexions (both of which depend on α), is utilized to adjust the intensities of the reflexions in the most satisfactory manner for photometry.

The standardization of the relative intensities may be made in two ways. A mixture method, such as we have previously described, may be used provided the particles of powder are sufficiently fine. In this case the mixture of KCl and a metal is photographed as above, and the setting of the plate and the composition of the mixture are chosen so that reflexions will be obtained of comparable intensities simultaneously from the KCl and the metal. The method has the advantage of eliminating consideration of absorption coefficients and does not require a steady output from the X-ray tube. Satisfactory mixtures, however, may be difficult or even impossible to obtain, and then the following method may be used.

The metal powder is placed in one cavity of the powder holder and KCl in the other cavity. Alternate exposures of metal and KCl are taken with the X-ray tube running under carefully controlled conditions. The photographs may be superimposed if convenient, or the photographic film may be raised slightly after each exposure, so that the final photograph shows alternate metal and KCl exposures developed and fixed under exactly the same conditions. The success of the method rests on the steady running of the X-ray tube, but this is possible if the exposures are not too long. Using a Philips's "Metalix Tube," we have found that the exposures required may be only a few minutes, or at the most about 20-30 minutes, and over such periods the tube can be operated steadily. Many modifications of this method are possible. One which we have found useful where long exposures are required is to superimpose the photographs of the two substances and to raise and

lower the specimen holder by means of a mechanical device every half minute. Actually, with the apparatus we have designed we can regulate the times of exposure of the two substances, *e. g.*, the powder holder may be up to expose one powder for 20 seconds and then down to expose the other powder for 35 seconds, and this process goes on mechanically throughout the exposure, which may last several hours. Where possible, however, we prefer short exposures with an alternate series of photographs side by side on the film.

4. Calculation of the Results.

It can be shown ⁽⁸⁾ that the total energy I_r reflected from a flat stationary layer of powder of effectively infinite thickness is given by the equation

$$I_r = \frac{I\lambda^3 e^4}{2m^2 c^4} \cdot \frac{pN^2 F^2}{\mu'} \left(\frac{1 + \cos^2 2\theta}{\sin \theta \sin 2\theta} \right) \frac{\rho'}{\rho} \left[\frac{\sin (2\theta - \alpha)}{\sin (2\theta - \alpha) + \sin \alpha} \right], \quad \dots (1)$$

which may be abbreviated to

$$I_r = (\text{constant}) \cdot \frac{pN^2 F^2 \rho'}{\mu' \rho} \phi(\theta) A, \quad \dots (2)$$

where

- p = multiplicity factor for the reflexion;
- N = number of unit cells per unit volume of crystal;
- F = amplitude scattered per unit cell;
- θ = glancing angle of reflexion;
- α = angle of setting of powder plate with respect to incident X-ray beam;
- μ' = effective linear absorption coefficient of powder block;
- ρ' = effective density of powder block;
- ρ = true density of the substance itself.

$\phi(\theta)$ is a convenient abbreviation for the trigonometrical functions, and A is a geometrical factor which takes into account the fact that different reflexions leave the powder block at different angles.

(i.) Relative Intensities and Relative Values of F .

For relative measurements from a stationary block of powder, equation (2) can be written as follows:—

$$I_r = (\text{constant}) \ p F^2 \phi(\theta) A. \quad \dots (3)$$

Nickel and copper have face-centred cubic lattices, so that $F=4f_T$, where f_T denotes the effective atomic scattering factor at temperature T . Zinc has a close-packed hexagonal structure; $F=Sf_T$ where S , the geometrical structure factor, equals 2, $\sqrt{3}$, and 1 for different types of reflexions (see Table VI.).

(ii.) *Standardization by the Mixture Method.*

Provided sufficiently fine particles can be obtained, a mixture of two powders can be assumed to have a common value of μ' , the linear absorption coefficient of the powder. If suffixes "1" and "2" relate to the two components of the mixture, then it is easy to show that

$$\frac{I_1}{I_2} = \frac{p_1 F_1^2 \phi_1(\theta) A_1 G_1 v_2 M_2}{p_2 F_2^2 \phi_2(\theta) A_2 G_2 v_1 M_1}, \quad \dots \quad (4)$$

where G denotes the weight of reflecting substance in the mixture, M the molecular weight of the unit cell, and v the volume of the cell. If two cubic crystals are compared, then in place of (v_1/v_2) we can write $(a_1/a_2)^3$ where a is the lattice spacing.

(iii.) *Standardization by the Method of Separate Powders.*

In this case we modify equation (2) by introducing the true linear absorption coefficient, μ ; since $\mu/\mu' = \rho/\rho'$, we can replace $\rho'/\mu'\rho$ by $1/\mu$. Then using suffixes "1" and "2" for the two substances, we obtain for the ratio of the reflected intensities for equal exposure times,

$$\frac{I_1}{I_2} = \frac{p_1 N_1^2 F_1^2 \phi_1(\theta) A_1 \mu_2}{p_2 N_2^2 F_2^2 \phi_2(\theta) A_2 \mu_1} \quad \dots \quad (5)$$

(iv.) *Temperature Correction.*

To obtain the true scattering factor, f , a correction for lattice vibration of the following kind is required:—

$$f_T = f e^{-M} \quad \dots \quad (6)$$

where

$$M = \frac{6h^2}{mk\Theta} \left[\frac{\Phi(x)}{x} + \frac{1}{4} \right] \left(\frac{\sin \theta}{\lambda} \right)^2, \quad \dots \quad (7)$$

where h is Planck's constant, k is Boltzmann's constant, m is the mass of the atom, Θ is the characteristic temperature which occurs in the theory of specific heats, $x = \Theta/T$

and $\Phi(x)$ is a function evaluated by Debye⁽¹⁰⁾. This form of the correction factor has been obtained by Debye⁽¹⁰⁾ and Waller⁽¹¹⁾ for cubic lattices*, but can probably be applied without serious error to a close-packed hexagonal lattice, since this lattice and a face-centred cubic lattice are two of the ways in which spherical atoms can be most closely packed. The characteristic temperatures of Ni, Cu, and Zn are as follows :—

Ni ⁽¹²⁾	$\Theta = 380^\circ$ Abs.
Cu ⁽¹³⁾	$\Theta = 315^\circ$ Abs.
Zn ⁽¹³⁾	$\Theta = 235^\circ$ Abs.

(v.) Scattering Factors for KCl.

James and Brindley⁽⁴⁾ have measured the scattering factor of KCl for MoK α radiation ($\lambda = 0.71$ Å.U.), and have applied a correction for secondary extinction. In applying these results to the reflexion of CuK α radiation from KCl, the desirability of making a dispersion correction must be considered. Renninger⁽¹⁴⁾ has recently considered the case of NaCl and has shown, on the basis of the theory developed by Hönl⁽⁵⁾, that the dispersion correction is very small. The correction may be represented as follows :—

$$f_\lambda = f_{\lambda \rightarrow 0} - \Delta f. \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Here Δf is the correction to be applied to $f_{\lambda \rightarrow 0}$, the scattering factor for very short wave-lengths, in order to obtain f_λ , the scattering factor for wave-length λ .

To obtain the scattering factor of KCl for CuK α radiation from the values obtained with MoK α radiation, two corrections are involved, which may be represented by the following equations :—

$$f(\text{MoK}\alpha) = f(\lambda \rightarrow 0) - \Delta f(\text{MoK}\alpha), \quad . \quad . \quad (9a)$$

$$f(\text{CuK}\alpha) = f(\lambda \rightarrow 0) - \Delta f(\text{CuK}\alpha), \quad . \quad . \quad (9b)$$

whence, by eliminating $f(\lambda \rightarrow 0)$, we obtain

$$f(\text{CuK}\alpha) = f(\text{MoK}\alpha) + \Delta f(\text{MoK}\alpha) - \Delta f(\text{CuK}\alpha). \quad . \quad (10)$$

There is, however, a further difficulty which arises from the manner in which the previous results for KCl

* Actually Waller made a slight modification of Debye's original expression by introducing an additional factor 2 into the expression for M. Equation (7) is Waller's modification of Debye's formula.

were corrected for extinction. This correction involved the use of the scattering factors for the (200) reflexion calculated theoretically from Hartree's wave-functions for K^+ and Cl^- and made the observed and calculated values agree for this reflexion*. Since the theoretically calculated scattering factors correspond to $\lambda \rightarrow 0$, the scattering factors given by James and Brindley for small angles of scattering where the extinction correction is important are the values for $\lambda \rightarrow 0$. The reflexions used in the present investigation, the (220), (420), and (422), lie in the region where the former extinction correction was appreciable; we shall therefore take them to be the appropriate values for $\lambda \rightarrow 0$, and will obtain the scattering factors for $CuK\alpha$ radiation by means of equation (9 b).

Using HönI's method, we find $-\Delta f(CuK\alpha)$ to be $+0.34$ for K^+ and $+0.32$ for Cl^- . Now Δf is the correction to be applied to the true scattering factor for a *stationary* atom; for an atom vibrating at temperature T , the appropriate correction is $\Delta f e^{-M}$. The factor e^{-M} is easily calculated from the following equation given by James and Brindley ⁽⁴⁾ † for M :—

$$M = \left(\frac{\sin \theta}{\lambda} \right)^2 8\pi^2 \left\{ 7.25 \times 10^{-5} T + \frac{0.1075}{T} - \frac{56}{T^3} \right\}.$$

The data which will be required are summarized in Table I. The second column gives values of the average scattering factor of K^+ and Cl^- obtained by interpolation from the results of James and Brindley; the fifth column gives the corrections to be applied at room-temperature (290° abs.), and the last column the corrected scattering factors for $CuK\alpha$ radiation at room-temperature.

The correction is seen to be of the order of 3 per cent. The uncertainties discussed above will have only a small

* The disadvantage of correcting for extinction in this way was fully realised when the original work was published and was pointed out as follows on p. 169. "This method of correcting for extinction... is not very satisfactory, in that it forces the observed and calculated curves to agree at one point. In the absence of any measured data for the extinction of KCl , it appears to be the best that can be done, and it should be emphasised that the agreement between theory and experiment for large angles of scattering is independent of any such correction." Reference to Table III. p. 165, of the original paper shows that the extinction correction is negligible beyond the (600) reflexion.

† See equation (10) of the paper by James and Brindley; we have here written $(\sin \theta)/\lambda$ in place of $(h^2 + k^2 + l^2)/4a^2$.

effect on this correction, and probably a negligible effect on our final scattering factors for Ni, Cu, and Zn. The discussion is given for the sake of completeness rather than because of its bearing on the final results.

5. The Question of Extinction.

In all measurements of X-ray intensities from powders, the question of the existence of appreciable extinction is of the greatest importance. With finely divided powders, primary extinction, due to the individual crystal fragments not being sufficiently small, is more likely to affect the results than secondary extinction, which depends on two or more fragments being set exactly parallel and in such a way that when reflexion occurs from one fragment

TABLE I.
Atomic Scattering Factors for KCl.

Spectra.	$f_T \left(\frac{K+Cl}{2} \right)$ (J. & B.).	$-\Delta f$.	e^{-M} .	$-\Delta f e^{-M}$.	$f_T(\text{CuK}\alpha)$.
220....	10.42	+0.33	0.917	+0.30	10.72
222....	8.82	+0.33	0.880	+0.29	9.11
420....	6.85	+0.33	0.807	+0.26	7.11
422....	6.10	+0.33	0.773	+0.25	6.35

the intensity falling on others is thereby reduced. With a well-mixed powder having no preferential orientation of the particles, secondary extinction is not likely to be important. Primary extinction, however, is exceedingly difficult to eliminate completely, because it necessitates the individual crystals being smaller than 10^{-4} cm. in size and preferably of the order of 10^{-5} to 10^{-6} cm. in size.

We have therefore made a separate examination of several kinds of KCl powders in order to test whether their reflexions are appreciably reduced by extinction. The results will be discussed in detail elsewhere*, and it will be sufficient to state here that the KCl powder precipitated from metallic potassium dissolved in alcohol exhibits practically no extinction. For the strongest spectrum, the (200), the decrease of intensity due to

* See subsequent paper by Brindley, Spiers, and Hoare, p. 1041.

extinction is less than 7 per cent., and the scattering factor is therefore diminished by less than $3\frac{1}{2}$ per cent. Assuming this effect to be wholly due to primary extinction, we find that the average crystal size is of the order of 5×10^{-5} cm. With crystals of this size primary extinction will have a negligible effect on all other reflexions than the (200).

6. Results.

1. Results for Nickel.

It follows from equation (3) that the measured reflexion intensities are proportional to $pF^2\phi(\theta)A$; in this

TABLE II.
Relative and Absolute Atomic Scattering Factors
for Ni. ($\lambda = 1.539$ Å.U.)

Spectra.	$(\sin \theta)/\lambda$ $\times 10^{-8}$.	p .	$\phi(\theta)$.	No. of films.	Expt. $pf_T^2\phi(\theta)$.	f_T (rel.).	f_T (abs.).	e^M .	$f(\text{abs.})$.
111 ..	0.246	8	5.685	7	502	3.33	14.9	1.025	15.3
290 ..	0.284	6	4.021	13	206	2.92	13.1	1.034	13.5 ₈
220 ..	0.402	12	1.758	—	100.0	2.18	9.8	1.068	10.4 ₈
311 ..	0.471	24	1.385	12	103.9	1.77	7.9 ₈	1.095	8.7
331 ..	0.619	24	3.024	18	80.2	1.05	4.7 ₈	1.170	5.5 ₈

expression, $pF^2\phi(\theta)$ depends only on the particular reflexion considered, but A depends also on the setting of the powder holder with respect to the X-ray beam. In presenting the relative intensity measurements, the factor A will be taken out because several settings of the powder block are always used for each group of lines compared. For nickel, which has a face-centred cubic lattice, $F = 4f_T$. The results for nickel are set out in Table II. The experimental values of $pf_T^2\phi(\theta)$ are given in the sixth column of the table, and in the fifth column are given the numbers of films which were measured for each determination. In the seventh column are given the *relative* values of the scattering factor f_T at room-temperature.

To obtain absolute values, both the mixture method and the method of separate exposures were used. By using both methods we can be certain that the final results will not be vitiated by errors arising in the use

of either method singly, and in particular we can verify that the powder particles were sufficiently fine to justify the use of the mixture method.

TABLE III.
Data for the Standardization of the
Results for Nickel.

	$f_T(\text{abs.})$.	$\frac{f_T(\text{abs.})}{f_T(\text{rel.})}$
I. <i>Mixture Method.</i>		
Ni (111) compared with KCl (220) gave $f_T(111)=14.7$		4.42
Ni (220) ,, ,, KCl (420) ,, $f_T(220)=9.7$		4.45
Ni (220) ,, ,, KCl (422) ,, $f_T(220)=10.1$		4.63
II. <i>Separate Exposure Method.</i>		
Ni (220) compared with KCl (420) gave $f_T(220)=9.9$		4.54
Ni (220) ,, ,, KCl (422) ,, $f_T(220)=9.8$		4.50

The absolute values of f_T given in Table III. when compared with the corresponding relative values in Table II. yield the following weighted average for the ratio of absolute to relative values:—

$$\frac{f_T(\text{absolute})}{f_T(\text{relative})} = \underline{\underline{4.49.}}$$

This conversion factor has been used to obtain the absolute f_T values in the eighth column of Table II. The ninth column gives the temperature factor e^M calculated from equations (6) and (7), and the final column gives the true scattering factor f corrected for lattice vibration.

II. Results for Copper.

These have been obtained in a manner exactly similar to that used for nickel. The results are tabulated in Tables IV. and V., and the absolute f_T and f values have been obtained in precisely the same way as above. There is excellent agreement between the ratio of absolute and relative values obtained by the mixture method and the separate exposure method; the average conversion factor is 5.43.

III. Results for Zinc.

Zinc, being an hexagonal crystal, gives many more reflexions than nickel and copper; the stronger reflexions only have therefore been measured. The standardization

TABLE IV.
Relative and Absolute Atomic Scattering Factors
for Cu. ($\lambda=1.539 \text{ \AA.U.}$)

Spectra.	$(\sin \theta)/\lambda$ $\times 10^{-8}$.	p .	$\phi(\theta)$.	No. of films.	Expt. $pf_T^2\phi(\theta)$.	f_T (rel.).	f_T (abs.).	e^M .	$f(\text{abs.})$.
111 ..	0.241	8	6.039	10	474.0	3.13	17.0	1.031	17.5
200 ..	0.278	6	4.279	12	204.0	2.82	15.3	1.042	15.9 ₅
220 ..	0.393	12	1.854	—	100.0	2.12	11.5	1.086	12.5
311 ..	0.461	24	1.415	8	104.0	1.75	9.5	1.121	10.6 ₆
222 ..	0.481	8	1.371	10	28.9	1.62	8.8	1.132	9.9 ₅
331 ..	0.605	24	2.392	13	81.0	1.18	6.4	1.218	7.8
420 ..	0.621	24	3.036	17	90.5	1.11	6.0	1.230	7.4

TABLE V.
Data for the Standardization of the Results for Copper.

I. <i>Mixture Method.</i>						$f_T(\text{abs.})$.	$\frac{f_T(\text{abs.})}{f_T(\text{rel.})}$.
(i.)	Cu (111)	compared with KCl (220)	gave $f_T(111)=17.1_0$	} 16.9 ₃		=17.0 ₅ =16.6 ₃	5.42
(ii.)	"	"	"				
(iii.)	"	"	"				
(i.)	Cu (200)	compared with KCl (220)	gave $f_T(200)=15.6_6$	} 15.3 ₁		=15.2 ₀ =15.0 ₈	5.44
(ii.)	"	"	"				
(iii.)	"	"	"				
II. <i>Separate Exposure Method.</i>							
(i.)	Cu (220)	compared with KCl (420)	gave $f_T(220)=11.7_1$	} 11.5 ₁		=11.3 ₀	5.43
(ii.)	"	"	KCl (422)				

TABLE VI.
Atomic Scattering Factor (relative values)
for Zinc. ($\lambda=1.539 \text{ \AA.U.}$)

Spectra.	$(\sin \theta)/\lambda$ $\times 10^{-8}$.	p .	S.	$\phi(\theta)$.	Expt. $pS^2f_T^2\phi(\theta)$.	No. of films.	f_T (rel.).
10I1	0.240	12	$\sqrt{3}$	6.005	869	9	2.00
10I2	0.298	12	1	3.580	114	9	1.63
10I3	0.374	12	$\sqrt{3}$	2.054	210	8	1.31
11I0	0.378	6	2	2.013			
11I2	0.429	12	2	1.556	100.0	—	1.16
20I1	0.448	12	$\sqrt{3}$	1.458	72.5	20	1.17
10I5	0.552	12	$\sqrt{3}$	1.571	53.1	11	0.63
11I4	0.554	12	2	1.588			
21I1	0.585	24	$\sqrt{3}$	1.971	74.4	13	0.72

of the intensities was carried out by the separate exposure method alone, since only a small quantity of zinc powder was available; the results given above for nickel and copper show that this method is quite reliable. The zinc results cannot be tabulated in exactly the same way as in the previous tables, because the geometrical structure factor S is different for different planes.

From the data in Table VII. we obtain the following weighted average for the ratio of the absolute to relative values :—

$$\frac{f_T(\text{absolute})}{f_T(\text{relative})} = \underline{\underline{9.70.}}$$

This conversion factor is now used to obtain absolute f_T and f values from the relative values given in Table VI.

TABLE VII.

Data for the Standardization of the Results
for Zinc. (Separate exposure method.)

					$f_T(\text{abs.}).$	$\frac{f_T(\text{abs.}).}{f_T(\text{rel.}).}$
(i.)	Zn (10 $\bar{1}$ 3)	+	(11 $\bar{2}$ 0)	compared with KCl (220)	$f_T(\text{abs.}). = 12.45$	12.6 ₃ 9.63
(ii.)	"	"	"	(420) " "	$= 12.51$	
(iii.)	"	"	"	(422) " "	$= 12.83$	
(i.)	Zn (11 $\bar{2}$ 2)		"	KCl (420) "	$f_T(\text{abs.}). = 10.98$	11.1 ₃ 9.63
(ii.)	"		"	(422) " "	$= 11.28$	
(i.)	Zn (20 $\bar{2}$ 1)		"	KCl (420) "	$f_T(\text{abs.}). = 11.44$	11.5 ₀ 9.85
(ii.)	"		"	(422) " "	$= 11.70$	

7. Discussion.

Tables II., IV., and VIII. give the results of measurements of the atomic scattering factors of Ni, Cu, and Zn at room-temperature (290° abs.), and the corrected scattering factors for the atoms at rest. In the case of Ni and Cu, the experimental values lie very well on the smooth curves drawn through the points; in the case of Zn, two of the experimental points (for the (2021) reflexion and the (1015)+(1124) reflexions), lie rather far off the mean curve. Additional measurements were made to test these values, and confirmed within the limits of experimental error the values given in Table VIII.

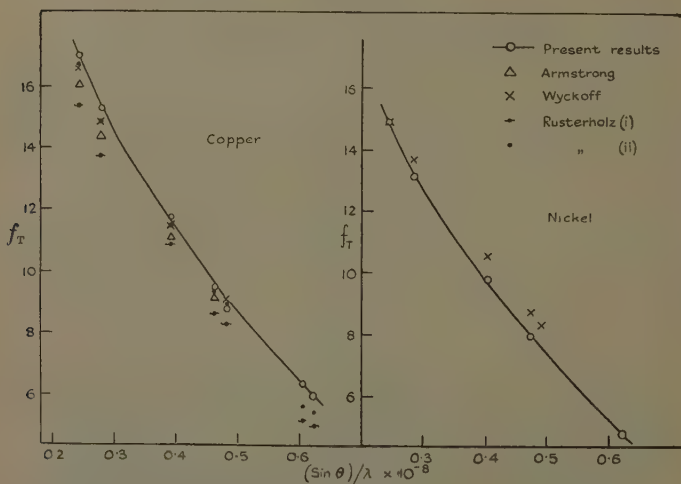
Previous measurements for copper have been made by Armstrong ⁽¹⁾, Wyckoff ⁽²⁾, and Rusterholz ⁽³⁾, and these

TABLE VIII.

Absolute Atomic Scattering Factors for Zinc.
($\lambda = 1.539 \text{ \AA.U.}$)

Spectra.	$(\sin \theta)/\lambda \times 10^{-8}$.	$f_T(\text{abs.})$.	e^M .	$f(\text{abs.})$.
10 $\bar{1}$ 1	0.240	19.4 ₅	1.044	20.3
10 $\bar{1}$ 2	0.298	15.8	1.069	16.9
10 $\bar{1}$ 3, 11 $\bar{2}$ 0..	0.376	12.7	1.112	14.2
11 $\bar{2}$ 2	0.429	11.2 ₅	1.148	12.9
20 $\bar{2}$ 1	0.448	11.4	1.161	13.2 ₅
10 $\bar{1}$ 5, 11 $\bar{2}$ 4..	0.553	6.1 ₅	1.257	7.7
21 $\bar{3}$ 1	0.585	7.0	1.292	9.0 ₅

Fig. 1

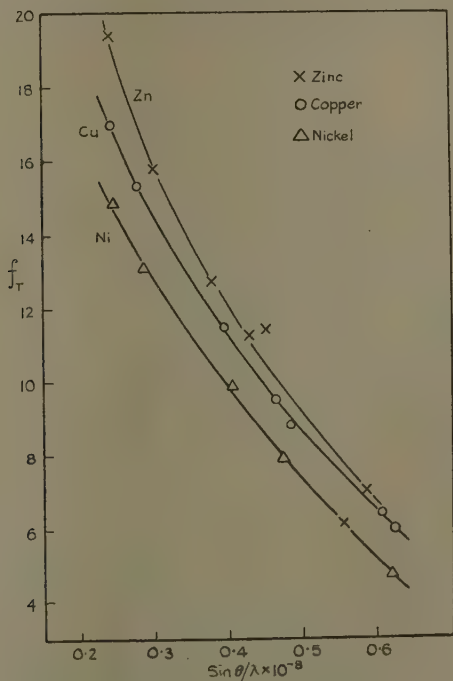


Atomic scattering curves for nickel and copper at room-temperature.
Comparison with results of previous investigators.

are compared with the present results in fig. 1. The experimental values of Miss Armstrong and Wyckoff are not independent; Wyckoff re-standardized the (220) spectrum but used Miss Armstrong's relative values. In his first paper Rusterholz ^(3a) gave a complete set

of scattering factors for copper with $\text{CuK}\alpha$ radiation, but these values are very low compared with the results of other observers. In his second paper Rusterholz^(3b) gives a value only for the (220) reflexion. We have therefore used the *relative* values given first by Rusterholz to obtain a second set based on his new standardization of

Fig. 2.



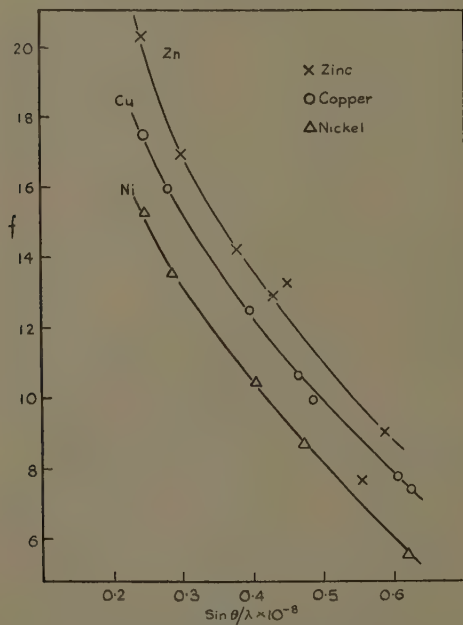
Atomic scattering curves for nickel, copper, and zinc at room-temperature.

the (220) reflexion; this second set is in much better agreement with our own results and those of Wyckoff, except for the (331) and (420) reflexions, for which Rusterholz's values appear to be low.

Previous measurements for nickel have been made by Wyckoff⁽²⁾, and they are compared with the present

results in fig. 1. The agreement is not good; Wyckoff's values are much higher than the present values, particularly for the higher order reflexions. Our results for Ni run parallel with those for Cu and Zn (see figs. 2 and 3), and it therefore seems unlikely that our values for Ni are much in error.

Fig. 3.



Atomic scattering curves for nickel, copper, and zinc, corrected for lattice vibration.

No previous measurements for zinc appear to have been made.

The present values for the scattering factors of Ni, Cu, and Zn at room-temperature are compared in fig. 2. It is seen that the scattering curve for Zn approaches very closely the curve for copper at large values of $(\sin \theta)/\lambda$ owing to the greater heat motion in the zinc lattice. When corrections are applied for lattice vibration,

the resultant scattering curves for the stationary atoms run much more nearly parallel; these results are shown in fig. 3.

Finally, it is with pleasure that we record our thanks to Professor Whiddington, F.R.S. for his interest in these experiments and for the use of a Cambridge microphotometer with which our films were measured, and to Mr. R. W. James, M.A., for kindly criticism. We also wish to thank the Government Grant Committee of the Royal Society for a grant with which necessary apparatus was purchased.

8. Summary.

The atomic scattering factors of nickel, copper, and zinc for $\text{CuK}\alpha$ radiation have been measured by the powder method using photographic recording of the X-ray reflexions. Absolute values of the reflected intensities have been obtained by comparison with reflexions from KCl. Two largely independent methods of comparison have been used which have given results in very close agreement. The results are compared with each other and, in the case of nickel and copper, with the results of previous observers. A temperature correction has been applied to the observed scattering factors at room-temperature to obtain the scattering factors for the atoms at rest.

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LXIX. *An X-ray Examination of Lattice Distortion in Copper and Nickel Powders.* By G. W. BRINDLEY, *M.Sc., Ph.D.*, and F. W. SPIERS, *Ph.D., Physics Laboratories, University of Leeds* *.

[Plate IX.]

1. *Introduction.*

AN investigation of the atomic scattering factors of several metals for copper $K\alpha$ -radiation has shown that the results depend to a considerable extent on the method of preparation of the powder for examination. In particular, powders prepared by a filing process give lower values than powders obtained by chemical precipitation or reduction. Measurement of this effect is important with regard to (1) determination of atomic scattering factors by the powder method; (2) any X-ray examination of alloys, in which case chemical methods of preparing the powder are not possible; and (3) the problem of the nature of distortion in metals. The filing process produces considerable distortions in the powder particles, and it will be shown that the observed lowering of the atomic scattering factors for the filed powders can be attributed to lattice distortions which are not present in the chemically prepared powders.

Hengstenberg and Mark ⁽¹⁾ have considered the effect of lattice distortion on the intensities of X-ray reflexions. Measurements made upon cold-worked metals (molybdenum, tantalum, tungsten, and duralumin) and upon a single crystal of KCl, subjected to pressure, lead them to the conclusion that at least part of the distortion consists of a random displacement of the atoms from their normal lattice positions. They considered that the effect of such displacement would be a lowering of the scattering factor similar to that produced by the heat motion of the lattice.

W. A. Wood ⁽²⁾ has studied the broadening of X-ray reflexions from cold-worked metals, and concludes that there is a definite limit to the amount of distortion which can be produced in a lattice. In his earlier papers ⁽²⁾ he also considers lattice distortion to be a random displacement of the atoms; in a later paper ⁽³⁾

* Communicated by Prof. R. Whiddington, F.R.S.

he concludes that an expansion of the lattice planes takes place when a metal is cold-rolled, and deduces from this expansion a value for the energy absorbed by the lattice when distorted to the limit. This idea of a maximum limit to the amount of energy absorbed is also put forward in a paper by Taylor and Quinney ⁽⁴⁾, who measure the energy expended in cold-working a metal.

The present investigations indicate that in filed powders the distortion is of the nature of a random displacement of the atoms of the lattice in accordance with the ideas of Hengstenberg and Mark. Measurement of the lowering of the scattering factor enables the average displacement of the atoms to be calculated, thus giving a quantitative figure for the distortion effect.

2. *Preparation of the Powders.*

(a) *Chemically prepared Powders.*—The copper was precipitated from copper sulphate solution, and the nickel obtained by the reduction of nickel formate in hydrogen in the same way as described in the preceding paper. The particle size in both cases was about 5×10^{-4} cm.

(b) *Filed Powder from a Chill-cast Copper Rod.*—For this purpose very pure electrolytic copper, estimated to be at least 99.95 per cent. pure, was melted in a fire-clay crucible and cast in an iron mould. A microphotograph of a section of the rod is shown in fig. 1 (Pl. IX.); the scale divisions at the side of the photograph are each 0.1 mm. and the size of the separate grains is shown to be about 10^{-2} cm. Powder was obtained by the use of a fine file, worked mechanically, and the smallest particles separated out with a 350 mesh sieve. Fig. 2 (Pl. IX.) shows that the average size of these particles is of the order of 2×10^{-3} cm. Each grain, therefore, produces approximately 5^3 particles, *i. e.* about a hundred. It is clear that in such a case the filing breaks up the original grains in an exceedingly drastic manner, and considerable strain and distortion might be expected to result from the process.

(c) *Filed Powder from a Hard-drawn Copper Wire (Gauge 0).*—We do not know the history of this wire, but believe it is of a high degree of purity. Microscopic

examination (see fig. 3, Pl. IX.) indicates a very small grain size, many times smaller than the particle size obtained by filing. The original grains will not be smashed up to the same extent as in the previous case, although they will have suffered much distortion in the hard-drawing process.

(d) *Filed Nickel Powder*.—This powder was filed from a strip of nickel of high purity. In its manufacture the strip had been hot- and cold-rolled, but subsequent treatment had been given to leave the nickel in a finely crystalline soft condition. Fig 4 (Pl. IX.) is a microphotograph of this nickel showing grains of the order of 5×10^{-3} cm., a figure still somewhat larger than the average size of the filed particles.

3. *Experimental Method.*

The measurements of the intensities of the X-ray reflexions were made by the same methods as those described in the previous paper. Only one point concerning the standardization of the results need be mentioned here; when discussing the accuracy of the mixture method, the necessity for using sufficiently small particles was emphasized in order to avoid errors due to absorption. It was found that the particles obtained by filing were much too large for this purpose and hence the method of separate exposures was used.

Relative intensity measurements for filed copper were first obtained, and then several of the reflexions were standardized against the precipitated copper powder by the method of separate exposures. In the case of nickel each reflexion was compared directly with the corresponding reflexion from the chemically prepared powder.

4. *Calculation of Results.*

For relative measurements from a stationary block of powder we can use equation (3) of the previous paper, which gives the total reflected energy I_r as

$$I_r = (\text{constant}) p F^2 \phi(\theta) A. \quad . \quad . \quad . \quad (1)$$

In the case of copper and nickel there are four atoms in the unit cube of the structure, so that if f_T is the

atomic scattering factor at a temperature T , $F=4f_T$ and we can write

$$I_r = (\text{constant}) p f_T^2 \phi(\theta) A. \quad . \quad . \quad . \quad (2)$$

For standardization by the separate exposure method we use equation (5) of the former paper and modify it for our present purpose. The equation is

$$\frac{I_1}{I_2} = \frac{p_1 N_1^2 F_1^2 \phi_1(\theta) A_1 \mu_2}{p_2 N_2^2 F_2^2 \phi_2(\theta) A_2 \mu_1}. \quad . \quad . \quad . \quad (3)$$

where suffixes 1 and 2 refer to the two substances.

However, in the present case we compare a given reflexion from the filed powder with the corresponding reflexion from the chemically prepared powder. Hence for any pair of lines so compared p , N , $\phi(\theta)$, A , and μ are the same for both powders, and remembering that $F=4f_T$ we can write equation (3) as

$$\frac{I_1}{I_2} = \left(\frac{f_{T1}}{f_{T2}} \right)^2. \quad . \quad . \quad . \quad . \quad (4)$$

5. Results for Copper Powders.

(1) Relative Values of f_T for Filed Copper Powders.

For each reflexion several settings of the powder holder are used, *i. e.*, several values of A are involved. In tabulating the results we have therefore taken out the A -factor and recorded the average values of I/A , which give the average values of $p f_T^2 \phi(\theta)$; these are set out in the sixth column of Table I., and in the seventh column are given the corresponding relative values of f_T . The third column indicates the total number of films on which each determination depends.

(2) Absolute Values of f_T for Filed Copper Powders.

Absolute values of f_T for filed copper powders were obtained for the spectra (220) and (311) by the separate exposure method. The calculations were made according to equation (4) and are set out in Table II. Column (3) gives the measured ratios of f_T for precipitated and filed copper. Column (4) gives the absolute values of f_T previously obtained for precipitated copper, and column (5) the absolute values of f_T now obtained for filed copper

TABLE I.

Relative Values of f_T for Filed Copper.

(a) From Chill-cast Copper Rod.

Spectra.	$(\sin \theta)/\lambda$ $\times 10^{-8}$.	No. of films.	p .	$\phi(\theta)$.	Expt. $pf_T^2\phi(\theta)$.	Filed copper. $f_T(\text{rel.})$.	$f_T(\text{abs.})$.	Pptd. copper. f_T .
111..	0.241	9	8	6.039	505.0	3.23	16.5	17.0
200..	0.278	7	6	4.279	202.0	2.81	14.4	15.3
220..	0.393	—	12	1.854	100.0	2.12	10.9	11.5
311..	0.461	10	24	1.415	104.3	1.75	8.9 ₅	9.5
331..	0.605	20	24	2.392	71.1	1.11	5.8	6.4
420..	0.621	18	24	3.036	69.9	0.98	5.0	6.0

(b) From Hard-drawn Copper Wire.

111..	0.241	12	8	6.039	479.0	3.15	16.8 ₅	17.0
200..	0.278	19	6	4.279	190.0	2.72	14.5	15.3
220..	0.393	—	12	1.854	100.0	2.12	11.3	11.5
311..	0.461	13	24	1.415	99.0	1.71	9.1 ₅	9.5
331..	0.605	10	24	2.392	63.8	1.05	5.6	6.4
420..	0.621	8	24	3.036	68.7	0.97	5.2	6.0

TABLE II.

Comparison of Absolute and Relative f_T Values
for Filed Copper.

1.	2.	3.	4.	5.	6.	7.
	Spectra.	$\frac{f_T(\text{pptd.})}{f_T(\text{filed})}$	$f_T(\text{pptd.})$ abs.	$f_T(\text{filed})$ abs.	$f_T(\text{filed})$ rel.	Ratio $\frac{(5)}{(6)}$
Chill-cast copper.	{ 220 311	1.064 1.059	11.5 9.5	10.8 9.0	2.12 1.75	5.10 5.14 } 5.12
Hard-drawn copper.	{ 220 311	1.028 1.024	11.5 9.5	11.2 9.2	2.12 1.71	5.29 5.41 } 5.35

Column (6) gives the relative f_T values for filed copper and column (7) the ratio of absolute to relative values of f_T for filed copper. These ratios are now used to convert the relative values of f_T in column (7) of Table I. to absolute values, which are recorded in the eighth column of that table. The values of f_T for precipitated copper are included in column (9) for purposes of comparison.

6. Results for Filed Nickel Powder.

Each reflexion from the filed nickel was compared directly with the corresponding reflexion from the chemically prepared powder. The absolute values of f_T for filed nickel, calculated by means of equation (4) are given in Table III. The values of f_T for the chemically prepared powder in column (5) are taken from the previous paper.

TABLE III.

Absolute Values of f_T for Filed Nickel Powder.

1.	2.	3.	4.	5.	6.
Spectra.	$(\sin \theta)/\lambda$ $\times 10^{-8}$.	No. of films.	$\frac{f_T(\text{filed})}{f_T(\text{chem.})}$	$f_T(\text{chem.})$.	$f_T(\text{filed})$.
111	0.246	9	0.983	14.9	14.6 ₅
200	0.284	9	0.963	13.1	12.6
220	0.402	15	0.970	9.8	9.5
311	0.471	9	0.960	7.9 ₅	7.6 ₅
331	0.619	18	0.935	4.7 ₅	4.4 ₅

7. Discussion.

An examination of columns (8) and (9) of Table I. and of columns (5) and (6) of Table III. shows that the f_T values for the filed powders are considerably less than the corresponding values for the chemically prepared powders. Moreover, the percentage difference between the two kinds of powders, although small for low order spectra, increases as we proceed to higher order spectra. For the copper (111) spectrum the decrease in f_T due to filing is about 2 per cent., but for the (420) spectrum the decrease has amounted to as much as 18 per cent.

In order to account for these results we now consider what kind of distortions are likely to be produced by the filing process. There are two kinds of distortions which can be considered easily in relation to the observed atomic scattering factors.

If the filing destroys part of the crystal lattice, producing a certain amount of amorphous material which would not contribute to the reflected intensities, we should expect the observed scattering factors to be reduced by a certain fraction which would be the same for all

spectra. This is clearly not the case, because the observed f_T is reduced much more for high order than for low order spectra.

The other type of distortion consists of a purely random displacement of the atoms from the points of the undisturbed lattice, which could be brought about by the straining of each particle as it is torn off in the filing process. In this case the atomic scattering factor would be changed according to the equation

$$f_T' = f_T e^{-M}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

where

$$M = \frac{8\pi^2}{3} (\sin \theta / \lambda)^2 \bar{u}^2, \quad . \quad . \quad . \quad . \quad . \quad (6)$$

and \bar{u}^2 is the mean square of the average atomic displacement; f_T is the scattering factor for the undistorted lattice and f_T' that for the distorted lattice. The expression for M in equation (6) has been derived in connexion with investigations of the effect of thermal vibrations on atomic scattering factors, and is equally applicable in the present case ⁽⁵⁾. This type of distortion will clearly affect the higher orders more than the lower orders, and so we now consider whether a suitable choice of \bar{u}^2 will account for the observed effects.

Since $M = \log(f_T/f_T')$, it is an easy matter to find the values of M for the different spectra, and so deduce the best value of \bar{u}^2 to fit the observed results. This has been done for copper (using the powder filed from the chill-cast rod) and also for nickel. The values so obtained for $\sqrt{\bar{u}^2}$ are

$$\text{Filed Copper} \dots \sqrt{\bar{u}^2} = 0.106 \times 10^{-8} \text{ cm.} \quad .. \quad (7)$$

$$\text{Filed Nickel} \dots \sqrt{\bar{u}^2} = 0.083 \times 10^{-8} \text{ cm.} \quad .. \quad (8)$$

Using these figures and applying the equations (5) and (6) to the values of f_T for the chemically prepared powders, we derive values of f_T' , which represent the scattering factors of copper and nickel for lattices in which the atoms have been randomly displaced by the amounts given in (7) and (8) respectively.

These results are collected together in Table IV., where the calculated values of f_T' are compared with the measured values for the filed powders.

The results can be represented graphically in two ways. In fig. 5 the values of f_T for both filed and chemically prepared powders are plotted as a function of $\sin \theta/\lambda$ in the usual way. The curves show the magnitude of the distortion effect and indicate that serious errors may arise in using powders which have been mechanically treated when determining atomic scattering factors.

TABLE IV.

(a) Observed and Calculated Scattering Factors for Filed Copper.

Spectra.	Observed values.		Calculated values. $f_T' = f_T e^{-M}$.
	Chill-cast.	Hard-drawn.	
111.....	16.5	16.8 ₅	16.9 ₅
200.....	14.4	14.5	15.0 ₅
220.....	10.9	11.3	11.0
311.....	8.9 ₅	9.1 ₅	8.9
331.....	5.8	5.6	5.7 ₅
420.....	5.0	5.2	5.3 ₅

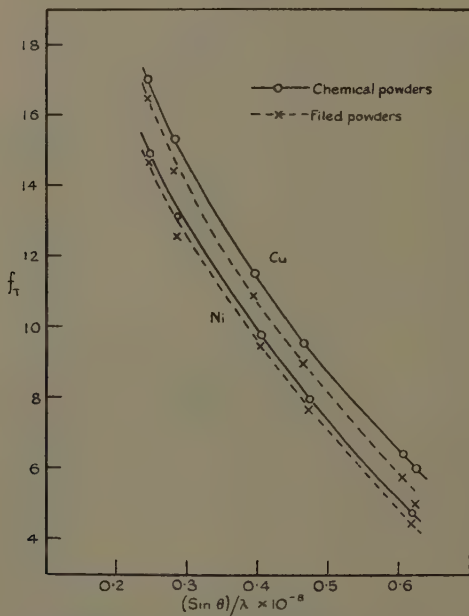
(b) Observed and Calculated Scattering Factors for Filed Nickel.

Spectra.	Observed values.	Calculated values. $f_T' = f_T e^{-M}$.
111.....	14.6 ₅	14.7 ₅
200.....	12.6	12.9
220.....	9.5	9.5
311.....	7.6	7.6 ₅
331.....	4.4 ₅	4.4 ₅

The distortion effect is, however, more clearly shown in fig. 6, where the ratio f_T (filed)/ f_T (chemical) is plotted against $\sin \theta/\lambda$. The continuous curves represent f_T'/f_T calculated from equations (5) and (6), where $\sqrt{u^2}$ is taken as 0.083 Å.U. for nickel and 0.106 Å.U. for copper. The graphs in fig. 6 are on a large scale, and tend to magnify the experimental errors. It will be seen, however, that the decrease in f_T for the filed powders

follows generally the course expected for a random displacement of the atoms in the manner suggested by Hengstenberg and Mark ⁽¹⁾. It is significant that the (200) reflexions from both powders give points which fall well below the curves. This may be an indication that the distortion effect is not entirely random, a point which is receiving further attention.

Fig. 5.



Atomic scattering factors for chemically prepared and filed powders of copper and nickel.

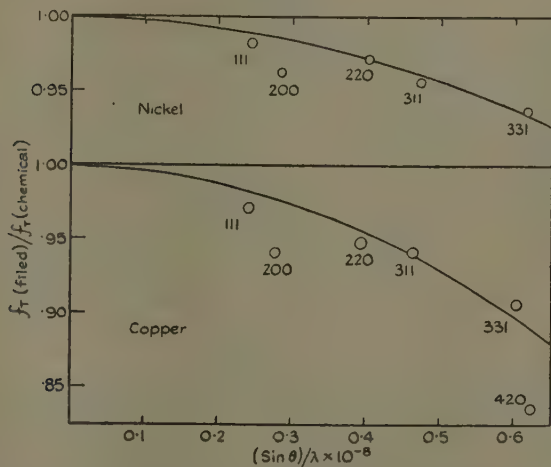
The (420) reflexion from copper is also very low, and this feature is in agreement with the measurements of line-width by Wood, which indicate that the (420) reflexion is much more susceptible to the effect of cold working than the (331) reflexion.

It is unlikely that extinction plays any part in the lowering of the (200) reflexion. The size of the filed

particles is certainly rather large, but extinction, if present in the (200) reflexion, should affect the (111) reflexion to an even greater extent. It might happen that the extinction effect is the same for both the filed and chemically prepared powders, but this, in view of the different particle size and mode of preparation, is very improbable.

It appears, therefore, that the nature of the distortion present in filed metal powders is mainly a random displacement of the atoms from their normal lattice positions, but with some preferential displacement

Fig. 6.



Lattice distortion in copper and nickel powders. The full lines represent $f_T'/f_T = e^{-M}$ where $M = 8\pi^2/3 \cdot (\sin \theta/\lambda)^2 \cdot \bar{u}^2$; $\sqrt{\bar{u}^2} = 0.083$ Å.U. for Ni and 0.106 Å.U. for Cu. The experimental values are shown by circles.

affecting the (100) planes more than any others. Wood^{(2), (3)} and Regler⁽⁶⁾ have shown that there is a fairly low limit to the amount of distortion which can be produced in a lattice, and that this limit is reached before the point at which recrystallization and preferred orientation sets in. Our present measurements give practically the same results for particles filed from two very different types of copper rod, one cast and therefore almost undistorted and the other hard-drawn, so that

the crystallites are already considerably strained. It is probable, therefore, that the particles we have examined have suffered the maximum amount of distortion possible and that the values we give will form useful criteria in discussing the intensities of X-ray reflexions from powders of these metals and their related alloys.

8. *Summary.*

Measurements are made of the atomic scattering factors of copper and nickel for copper $K\alpha$ -radiation, using chemically prepared and filed powders. The values for the filed powders are definitely less than those for the chemically prepared powders, and the extent of the lowering is found to increase with the order of the spectrum. This effect is attributed to lattice distortion caused by filing, and it is shown that the results can be explained on the assumption that the distortion is a random displacement of the atoms from the points of the undistorted lattice. The magnitude of the displacement is found to be 0.106 Å.U. for copper and 0.083 Å.U. for nickel. Scattering factors for the (200) reflexions from both filed powders are reduced much more than can be explained in this way, and this may mean that the distortion of the lattice is not entirely random.

9. *Acknowledgments.*

We wish to thank Prof. Whiddington for his interest in this work and for facilities for photometering the films. We are much indebted to Mr. A. Preece, M.Sc., of the Metallurgy Department of the University, for the very valuable assistance he has so freely given us in connexion with the micrographical study of the metals used, and to the Government Grant Committee of the Royal Society for a grant with which necessary apparatus was bought. Finally, we wish to thank Messrs. Thomas Bolton and Sons for some very pure electrolytic copper, and the Mond Nickel Company, Limited, for a suitable piece of highly pure nickel.

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LXX. *An X-ray Investigation of Lattice Distortion in a Copper-Beryllium Alloy.* By G. W. BRINDLEY, M.Sc., Ph.D., and F. W. SPIERS, Ph.D., *Physics Laboratories, University of Leeds* *.

[Plate X.]

1. *Introduction.*

THE method of measuring lattice distortions in metals described in the preceding paper has been applied to the case of an alloy consisting of a solid solution of beryllium in copper. In an alloy of this kind we may expect to find lattice distortions arising from the introduction of foreign atoms into the lattice of the pure metal. The alloy we have examined contained 0.72 per cent. beryllium by weight and was kindly presented to us in the chill-cast condition by Messrs. James Booth and Co., Ltd., of Birmingham.

The phase-diagram of the CuBe system has been studied by Oesterheld ⁽¹⁾, and more recently by Dahl, Holm and Masing ⁽²⁾ using X-ray methods. According to the latter investigators, the α -phase is a solid solution of beryllium in copper extending at ordinary temperatures up to approximately 0.7 per cent. Be by weight (5 atomic per cent.). Beyond this composition, there is a mixture of α - and γ -phases which continues up to approximately 11.2 per cent. Be by weight (47 atomic per cent.). The alloy we have used lies just on the boundary of the α - and ($\alpha + \gamma$) regions. The X-ray photographs indicated that the alloy was homogeneous, and no trace of the γ -phase was observed.

A microscopic examination of the alloy showed that the individual grains were large, of the order of $\frac{1}{2}$ mm.—1 mm. in size, and that the grain boundaries were very fine; a typical microphotograph is shown in fig. 1 (Pl. X.), with a scale of 1/10 mm. attached.

* Communicated by Prof. R. Whiddington, F.R.S.

Owing to the large size of the grains, it was not possible to carry out the investigation directly with the chill-cast alloy; a metal with such a coarse grained structure would give extremely spotty lines in an X-ray photograph, and these would be quite useless for making intensity measurements. By suitably cold-working the metal, *e.g.*, by rolling, a fine grained structure might be obtained which would give uniform X-ray lines suitable for intensity measurements, but such a process would introduce additional distortions and would also produce a preferential orientation of the lattice planes which would complicate enormously the interpretation of the X-ray intensities. Suitable annealing might remove the distortions produced by the mechanical treatment, but this would probably lead to new crystal growth and again give spotty X-ray lines, and in any case the preferential orientation of the lattice planes would probably remain to some extent. In view of these considerations, it appears simpler in the first place to produce a finely powdered alloy by filing, and then to estimate the effect of the filing by considering the corresponding results for the pure metal. Experiments are in progress to examine how far strains induced in a metal by filing can be removed by an annealing treatment without the production of relatively large crystals; such experiments must, however, be carried out in the first place with pure metals which can be obtained in a finely divided state by chemical precipitation.

2. *Experimental Method.*

The method of investigation was essentially the same as that described in the preceding papers. The intensities of the X-ray reflexions from the powdered alloy were compared with the corresponding reflexions from pure copper powder obtained by chemical precipitation. The two cavities of the powder holder were filled with the alloy and with copper, and X-ray photographs were taken alternately of the two powders in the manner previously described. Since the small percentage of beryllium in the alloy has an almost negligible effect on the lattice spacing (the change is only 0.2 per cent.), the reflexions from the alloy occur at practically the same angles as from copper. Each reflexion from the alloy was therefore compared directly with the corresponding reflexion

from copper. Fig. 2 (Pl. X.) is a reproduction of a typical photograph; the alloy received twice the exposure time given to the copper in order to compensate for the weakened reflexions and yield lines of comparable densities for photometry. The photographs were taken with $\text{CuK}\alpha$ radiation from a Philips "Metalix Tube," the output of which was kept constant by a careful control of the filament current and high tension during the exposures; these lasted from periods as short as a few minutes to periods as long as 20 minutes for the weakest reflexions.

3. Calculations.

The calculations involved are similar to those given previously. The ratio of the intensities reflected by two powders irradiated for the same periods of time is given by the equation

$$\frac{I_1}{I_2} = \frac{p_1 N_1^2 F_1^2 \phi_1(\theta) A_1 \mu_2}{p_2 N_2^2 F_2^2 \phi_2(\theta) A_2 \mu_1} \quad (1)$$

where the suffixes "1" and "2" refer to the two substances.

In the present connexion, this equation can be considerably simplified. When comparing the *same* reflexions from the alloy and from copper, p , $\phi(\theta)$, and A will be the same for both powders. Since both crystals are cubic, we can write in place of N , the number of unit cells per unit volume, $1/a^3$, where a is the side of the unit cube; then N_1/N_2 becomes $(a_2/a_1)^3$. Also, since both lattices are face-centred cubic, F , the amplitude scattered per unit cell, is equal to $4f_T$, where f_T is the atomic scattering factor at room-temperature. Making these substitutions, we can write equation (1) as follows:—

$$\left(\frac{f_{T1}}{f_{T2}} \right)^2 = \frac{I_1 \mu_1}{I_2 \mu_2} \left(\frac{a_1}{a_2} \right)^6 \quad (2)$$

For the ratio (a_1/a_2) we take the figures given by Dahl, Holm, and Masing⁽²⁾. They have measured the lattice spacings of several copper-beryllium alloys in the α -phase; from their data we obtain by interpolation the value 3.603 Å.U. for the lattice spacing of our alloy. The same investigators give for pure copper a value 3.619 Å.U. Although these figures may not be exactly correct, the ratio is probably accurate, and this is what is required

in the present work. The linear absorption coefficient of the alloy is easily obtained in the usual way from the mass absorption coefficients of the separate atoms and the composition of the alloy; we find that μ for the alloy is 446.8 and for copper is 470.7. If now we let suffix "1" represent the alloy and "2" copper, then on substituting numerical values in equation (2) we obtain

$$\frac{f_T(\text{CuBe})}{f_T(\text{Cu})} = \left(\frac{I(\text{CuBe})}{I(\text{Cu})} \right)^{1/2} \times 0.962. \quad . \quad . \quad (3)$$

4. Experimental Results.

The experimental values for the ratio $[I(\text{CuBe})/I(\text{Cu})]$ and the number of films on which each determination

TABLE I.
Experimental Data for Intensities of X-ray
Reflexions from CuBe.

1. Spectrum.	2. ($\sin \theta/\lambda$) $\times 10^{-8}$.	3. No. of films.	4. $\frac{I(\text{CuBe})}{I(\text{Cu})}$.	5. $\frac{f_T(\text{CuBe})}{f_T(\text{Cu})}$.	6. $f_T(\text{Cu})$.	7. $f_T(\text{CuBe})$.
111	0.241	8	0.883	0.903	17.0	15.3 ₅
200	0.278	7	0.863	0.893	15.3	13.6 ₅
220	0.393	12	0.807	0.864	11.5	9.9 ₅
311	0.461	8	0.805	0.863	9.5	8.2
331	0.605	9	0.721	0.817	6.4	5.2 ₅

depends are given in columns (3) and (4) of Table I. Columns (1) and (2) give the indices of the reflexions and $(\sin \theta/\lambda) \times 10^{-8}$. Column (5) gives the values of $[f_T(\text{CuBe})/f_T(\text{Cu})]$ calculated by means of equation (3). Column (6) gives the values of f_T for copper obtained previously, and column (7) gives the corresponding values of f_T for the alloy.

5. A Comparison of Experimental and Calculated Scattering Factors for CuBe.

In order to obtain information about the distortions in CuBe, we must now calculate the scattering factors for the ideal alloy having no distortions from the known scattering factors of copper and beryllium. This involves calculating f , the average atomic scattering factor for the

atoms *at rest* in the alloy, and the temperature factor for the alloy in order to correct for the lattice vibration at room-temperature. Actually both these calculations entail only small corrections in the corresponding values for copper, and so they can be obtained with sufficient accuracy.

The scattering factor at temperature T , f_T is related to the scattering factor for the stationary atom, f , by the equations

$$f_T = f \cdot e^{-M} \text{ where } M = \frac{6 \hbar^2}{mk\Theta} \left[\frac{\Phi(x)}{x} + \frac{1}{4} \right] \left(\frac{\sin \theta}{\lambda} \right)^2 \quad (4)$$

and $x = \Theta/T$. The notation used here has been explained in the preceding papers.

The composition of the alloy by weight is 0.72 per cent. Be, 99.28 per cent. Cu. Taking the atomic weights as 9.02 for Be and 63.57 for Cu, we find the relative numbers of atoms to be 4.9 per cent. Be and 95.1 per cent. Cu. If the two kinds of atoms are randomly distributed, then

$$f(\text{CuBe}) = 0.951 \cdot f(\text{Cu}) + 0.049 \cdot f(\text{Be}). \quad (5)$$

For $f(\text{Cu})$ we shall use the values given in the first of the two preceding papers and for $f(\text{Be})$ we can use the values given by James and Brindley ⁽³⁾.

The calculation of the temperature factor e^{-M} for the alloy can be carried out approximately as follows:—The substitution of Be for Cu atoms will affect M in two ways; the mass, m , of the average atom is less in the alloy than in copper, and the characteristic temperature Θ , may be changed. The average value of m for the alloy is easily obtained from the average atomic weight, \bar{A} , which is given by

$$\bar{A} = (0.049 \times 9.02) + (0.951 \times 63.57) = 60.90.$$

We have no data from which to calculate the change of Θ , but since the melting-point of the alloy (about 1050° C.) differs very little from that of pure copper, 1083° C., the change of Θ is probably small and its effect on e^{-M} may be neglected. For pure copper, $\Theta = 315^\circ \text{ Abs.}$ In this way we obtain the following:—

$$\left. \begin{array}{ll} \text{For pure copper} & \dots \quad M = 0.541 \cdot (\sin \theta / \lambda)^2 \\ \text{For CuBe alloy} & \dots \quad M = 0.565 \cdot (\sin \theta / \lambda)^2 \end{array} \right\} \quad (6)$$

In these expressions for M , λ is measured in Å.U. The slightly higher value of M for the alloy may be regarded qualitatively as due to the lighter Be atoms having a larger amplitude of vibration than the heavier Cu atoms for a given energy of vibration.

Using equations (4), (5), and (6) we can now calculate the scattering factors for the ideal undistorted alloy at room-temperature. The necessary data are set out in Table II. Column (1) gives the spectra for which results have been obtained; column (2) gives the scattering factors of copper previously obtained; column (3) the scattering factors of beryllium given by James and Brindley⁽³⁾; column (4) the scattering factors of CuBe calculated by means of equation (5); column (5) the temperature

TABLE II.
Calculation of f for CuBe Alloy.

1. Spectra.	2. $f(\text{Cu})$.	3. $f(\text{Be})$.	4. $f(\text{CuBe})$.	5. $e^{-M}(\text{CuBe})$.	6. $f_T(\text{CuBe})$.
111	17.5	1.81	16.7 ₅	1.033	16.2
200	15.9 ₆	1.75	15.2 ₆	1.044	14.6
220	12.5	1.55	12.0	1.090	11.0
311	10.6 ₈	1.45	10.1 ₆	1.127	9.0
331	7.8	1.20	17.4 ₅	1.228	6.0 ₆

factors for CuBe calculated from equation (6); column (6) the scattering factors of CuBe at room-temperature. Since $f(\text{Be})$ is small compared with $f(\text{Cu})$, and since only about 5 per cent. of the atoms in the alloy are Be atoms, the Be atoms contribute very little to the average scattering factor for the alloy; in consequence, any small error in $f(\text{Be})$ will have no appreciable effect on $f(\text{CuBe})$.

Column (7) of Table I. gives the observed scattering factors for the distorted alloy, and column (6) of Table II. gives the scattering factors for the ideal alloy free from distortion. A comparison of these two sets of results should give us information regarding the distortions in the actual alloy. The ratios of the observed and calculated scattering factors are given in Table III.

6. Discussion.

In the case of nickel and copper we have been able to show that the experimental results are consistent with

the view that filing produces an approximately random displacement of the atoms from the lattice points. In the case of the powdered alloy two possibilities have to be considered. In the first place, the formation of the powder by filing will probably produce lattice distortions similar to those produced in pure copper and nickel. Secondly, additional distortions may be expected arising from the presence of the beryllium atoms.

If the effect of the beryllium atoms is on the average to produce a random displacement of the atoms from the lattice points, then the variation of the ratio $[f_1(\text{CuBe, Expt.})/f_T(\text{CuBe, Ideal})]$ with $(\sin \theta)/\lambda$ should be of the form e^{-M} where $M=b(\sin \theta/\lambda)^2$ and from b the root mean square displacement can be calculated: $b=8\pi^2 \cdot \overline{u^2}/3$

TABLE III.

Comparison of Experimental and Calculated
Scattering Factors for CuBe.

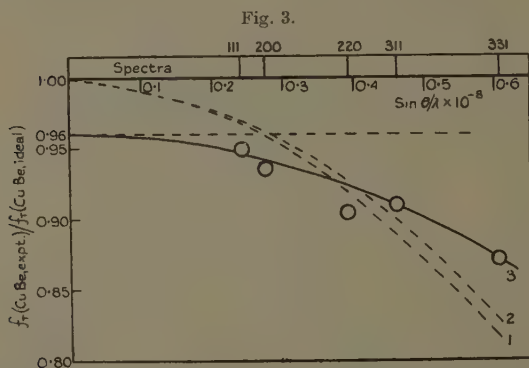
Spectra.	$(\sin \theta)/\lambda$ $\times 10^{-8}$.	$f_T(\text{CuBe, Expt.})$ $f_T(\text{CuBe, Ideal})$.
111	0.241	0.95
200	0.278	0.93 ₆
220	0.393	0.90 ₅
311	0.461	0.91
331	0.605	0.87

where u^2 is the mean square displacement ⁽⁴⁾. The experimental values of this ratio are plotted against $(\sin \theta)/\lambda$ in fig. 3, where they are shown by circles. The dashed lines in this figure represent the function e^{-M} with $M=0.50 (\sin \theta/\lambda)^2$ and $M=0.55 (\sin \theta/\lambda)^2$. It is obvious from the way these two curves run with respect to the experimental points, that they cannot be fitted even approximately by a curve of the form e^{-M} passing through the origin of the diagram.

If, however, a smooth curve is drawn as well as possible through the experimental points and extrapolated back to $(\sin \theta)/\lambda=0$, then it cuts the vertical axis at about 0.96. This is shown by the full curve in fig. 3, which is actually the curve e^{-M} with $M=0.25 (\sin \theta/\lambda)^2$ drawn through the point 0.96 as origin. The experimental

points fit this curve within the limits of experimental error. From the constant, 0.25, we can calculate the root mean square displacement; in this way we obtain $\sqrt{u^2} = 0.090$ Å.U., which is of the same order of magnitude as the result previously obtained for copper.

We have now to consider what is the significance of the result that the ratio $[f_T(\text{CuBe, Expt.})/f_T(\text{CuBe, Ideal})]$ can be fitted by a curve of the type e^{-M} if the value of the ratio is increased by about 4 per cent., for this is what is implied by taking the origin at 0.96 on the vertical axis. It is possible that the decrease of the ratio according to an e^{-M} law arises from the filing process and that the



Lattice distortion in CuBe alloy.

Curves 1 and 2 represent the expression e^{-M} with $M = 0.55 (\sin \theta/\lambda)^2$ and $M = 0.50 (\sin \theta/\lambda)^2$. Curve 3 represents e^{-M} with $M = 0.25 (\sin \theta/\lambda)^2$ and passing through the ordinate 0.96 as origin. The experimental values are shown by circles.

additional 4 per cent. reduction is connected with the presence of the beryllium atoms in the lattice.

The exact nature of solid solutions is still not completely understood. When the proportion of the dissolved constituent, Be in this case, is increased beyond a certain limit, a mixture of phases is formed; thus in the CuBe phase diagram we pass from a region where the α -phase alone is present to a region where there is a mixture of $(\alpha + \gamma)$ -phases, and the composition at which the γ -phase first makes its appearance is fairly well defined. In order, however, that the γ -phase shall give lines in an

X-ray photograph, there must be regions in the alloy extending over at least 100 atoms which have the γ type of structure. Now the alloy we have used gives X-ray reflexions corresponding to the α -phase alone, but its composition is very near the limit where the γ -phase first appears. There may then be an incipient tendency towards a building up of the γ -phase which is never quite complete or extensive enough to yield X-ray reflexions characteristic of the γ -phase, but is sufficient to withdraw effectively certain atoms from the α -phase. Such a process would lead to a fractional reduction of the average atomic scattering factor for the alloy and would be in accordance with the results of this investigation. We put forward this hypothesis tentatively until more experimental results have been accumulated for other alloys.

7. Summary.

Using methods previously described, the average atomic scattering factor has been determined experimentally for a CuBe alloy containing 0.72 per cent. Be by weight. The results are compared with the scattering factor calculated for the ideal undistorted alloy. The experimental values are less than the calculated values, and the difference increases with the order of the reflexion. This is attributed to lattice distortion in the alloy arising partly from the filing process by which the alloy was obtained as a fine powder suitable for X-ray measurements, and partly from the presence of Be atoms in the lattice. The ratio of the observed to the calculated scattering factors can only be partially explained in terms of a random displacement of the atoms from the lattice points; this probably arises mainly from the filing process, for similar results were obtained with the pure metals, copper and nickel. In addition to the lowering of the observed scattering factor due to a random atomic displacement, it appears that the scattering factors are also lowered by about 4 per cent. and this, it is suggested, may be due to the effect of the Be atoms in the lattice; a tentative explanation is given.

8. Acknowledgments.

Finally, we wish to thank Prof. Whiddington for his interest in these experiments and for the use of a Cam-

bridge microphotometer, purchased out of a Royal Society grant, with which out photographs were measured. We also wish to thank Messrs. James Booth and Co. Ltd., of Birmingham, for the gift of the CuBe alloy with which our experiments were carried out. We are indebted to the Government Grant Committee of the Royal Society for a grant with which part of the necessary apparatus was purchased.

References.

- (1) G. Oesterheld, *Zeit. f. anorganischen Chem.* xcvi. p. 6 (1916).
- (2) O. Dahl, E. Holm, and G. Masing, *Wiss. Veröff. a.d. Siemenskonzern*, viii. p. 154 (1929).
- (3) R. W. James and G. W. Brindley, *Phil. Mag.* xii. p. 81 (1931); *Zeit. f. Krist.* lxxviii. p. 470 (1931).
- (4) This expression for b has been given by Waller; see I. Waller and R. W. James, *Proc. Roy. Soc. A*, cxvii. p. 214 (1927).

LXXI. *Collisions of Slow Electrons with Methane Molecules.*
 By HENRY L. BROSE, M.A., D.Phil.(Oxon), D.Sc.,
Lancashire-Spencer Professor of Physics, and JOHN E.
 KEYSTON, D.Phil.(Oxon), B.Sc., *University College*,
Nottingham *.

1. **T**HE type of apparatus used in this research has been described in earlier communications to the 'Philosophical Magazine' †. By measuring the distribution of electronic currents over the three receiving electrodes when moving under uniform electric force it is possible to determine the average velocity of agitation U of the electrons in their irregular paths while drifting as a whole towards the electrodes. By superimposing a transverse magnetic force upon the uniform electric force the average velocity of drift W of the electrons in the direction of the electric force Z may also be determined. It was shown in the first experiments of this kind by Townsend and Bailey that these electronic velocities U and W depend only on the ratio of the uniform electric force Z to the gas pressure p , provided that the electrons do not form ions while passing through the gas. In cases where ions are formed

* Communicated by the Authors.

† J. S. Townsend and V. A. Bailey, *Phil. Mag.* xlii. p. 873 (1921); H. L. Brose and E. H. Saayman, *Ann. d. Phys.* (5) v. p. 797 (1930).

it is generally necessary to apply one of the methods suggested by V. A. Bailey *. The mean free path of the electrons in the gas at a pressure of 1 mm. of Hg is calculated from U and W by means of the formula

$$L = \frac{7WU \cdot 10^{-16}}{Z/p}, \dots \dots \dots (1)$$

where

W=Drift velocity of the electrons in cm./sec.

U=Velocity of agitation of the electrons in cm./sec.

Z=Uniform electric force in volt/cm.

p=Gas-pressure in mm. of Hg.

L=Mean free path in cm.

The reciprocal of L is called the effective cross-section of the gas atoms or molecules with respect to electrons of average velocity of agitation U, and is denoted by Q :

$$Q = \frac{1}{L} = \frac{Z/p \cdot 10^{16}}{7WU} \dots \dots \dots (2)$$

Q is expressed in cm.²/cm.³. Concerning the agreement between this Q and the "Wirkungsquerschnitt" (Q_{wirk}), determined by Ramsauer and his collaborators, see Brose and Saayman, *loc. cit.*, and also a more recent paper by Brose † which discusses the implications of the definition of cross-section. The velocity of agitation U is derived from the Townsend temperature factor k , which expresses the ratio of the mean energy of agitation (or mean thermal energy) of the electrons to the mean energy of agitation of the molecules of the gas at 15° C. The formula connecting U and k is

$$U = 1.15 \cdot 10^7 \sqrt{k} \dots \dots \dots (3)$$

Moreover, since

$$U = 5.94 \cdot 10^7 \sqrt{V} \dots \dots \dots (4)$$

for the slow electronic velocities here in question, we have

$$V = \frac{k}{27} \dots \dots \dots (5)$$

With the help of these relationships we may express Q in terms of the velocity of the electrons expressed in $\sqrt{\text{volts}}$.

* V. A. Bailey, *Phil. Mag.* i. p. 825 (Oct. 1925).

† H. L. Brose, *Ann. d. Phys.* xvii. p. 816 (1933).

The only essential improvements embodied in the present apparatus consisted in the improved insulation (amber instead of pyrex wherever possible) and in an improved switch system for connecting the receiving electrodes with the condensers and the electrometer. The source of light used for releasing photo-electrons from the lower side of the top plate was a tungsten arc in air, which was found to have advantages over the condensed spark, particularly at low values of Z/p .

2. Two samples of methane were used in these experiments. One was obtained from a special cylinder of methane of 99.9 per cent. purity, which was kindly supplied to us by Prof. McMillan, Head of the Mining Department; the other was prepared by the action of steam on pure aluminium carbide. The gas evolved by the carbide was passed successively through flasks containing ammoniacal cuprous chloride, concentrated sulphuric acid, potassium hydroxide, alkaline hyposulphite, and again concentrated sulphuric acid. Hydrogen was removed by passing the gas over heated copper filings. The gas was finally dried for several days by means of phosphorus pentoxide. In the subsequent measurements made on the cylinder gas and on that obtained from the carbide the results obtained were found to be the same. The cylinder gas had been dried by being passed over potassium hydroxide and phosphorus pentoxide.

3. Table I. exhibits the values obtained for k and W corresponding to Z/p for different values of Z and p . It will be seen that for a given value of Z/p the values of k show a tendency to decrease as the pressure is increased; this arises from the formation of ions in the gas at higher pressures. The value of k for a stream of ions is unity, and hence, since the number of ions formed in the gas increases with the number of collisions, and therefore with the pressure, the highest values of k are to be expected for the lowest values of p at a given value of Z/p . In the case of the elementary gases it has been shown that the formation of ions is due to the presence of minute traces of impurity in the gas*; in the case of the compound gases, however, the formation of ions by the attachment of electrons to the molecules of the gas becomes added.

* H. L. Brose, *Phil. Mag.* i. p. 536 (1925).

Ion formation was observed in the case of ethylene by Bannon and Brose *. Bailey and his collaborators in Sydney have succeeded in measuring the coefficient of attachment of electrons to gas molecules in several gases,

TABLE I.

Z.	p .	Z/p .	k .	W.
1.2	21.2	.057	2.3	6.64
2.2	21.2	.104	2.56	18.62
1.2	10.7	.112	3.0	
2.1	10.12	.207	2.88	24.25
1.0	4.96	.202	3.7	
4.2	9.64	.436	2.92	52.57
2.1	4.64	.453	4.66	
10.25	9.64	1.06	7.2	85
5.0	4.88	1.024	8.33	
2.55	2.5	1.02	9.31	
20.75	9.64	2.16	15.1	102.6
10.2	5.26	1.94	17.0	
10.1	4.68	2.16	17.4	
5.1	2.46	2.07	18.54	
5.0	2.46	2.03	18.87	
41.6	9.64	4.33	34.66	107.3
20.2	4.68	4.32	35.14	
10.8	2.46	4.39	43.2	
35.0	5.26	6.65	58.33	108.6
16.25	2.42	6.72	65.0	
40.6	5.26	7.72	63.42	108.7
20	2.56	7.81	72.72	
31	2.46	12.6	112.73	
43	2.56	16.8	143.3	

including pentane †, which might be expected to behave similarly to methane.

The total ionic current in the gas may be measured by applying a horizontal magnetic field strong enough to

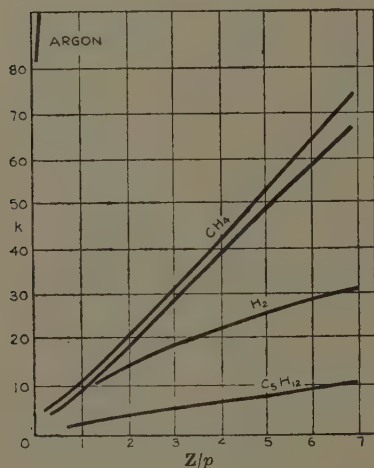
* J. Bannon & H. L. Brose, *Phil. Mag.* vi. p. 1107 (1928).

† V. A. Bailey and W. E. Duncanson, *Phil. Mag.* x. p. 145 (1930); J. D. McGee and J. C. Jaeger, *Phil. Mag.* vi. p. 1107 (1928).

deflect all the electrons away from the electrodes ; in the case of methane this current was found to amount to not more than 3 per cent. of the total electronic current. The presence of ions caused similar but smaller variations in the values obtained for W . For this reason W was, for most values of Z/p , measured only at the lowest pressures, corresponding to the highest values of k .

The curve connecting Z/p and k for methane is shown in fig. 1. The corresponding curves for argon and pentane

Fig. 1.



are also shown for comparison. The curve marked k_{ex} has been plotted from values of k which are obtained by extrapolating the various values of k for a constant value of Z/p to zero pressure. This extrapolation, an example of which is given in fig. 2, has no strict theoretical basis ; it indicates the extreme upper limit which the value of k may attain for a given value of Z/p , and serves to show to what extent the results are influenced by variations in the values of k owing to the formation of ions.

The curves connecting Z/p and W for methane, pentane, and argon are given in fig. 3. The similarity in the shape of the curves for methane and pentane is particularly

striking. Table II. contains values of Z/p , k , k_{ex} , and W , together with the calculated values of U , \sqrt{V} , L , Q , and λ . λ is the average fraction of the energy lost by an electron

Fig. 2.

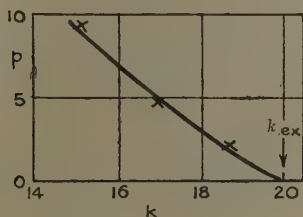
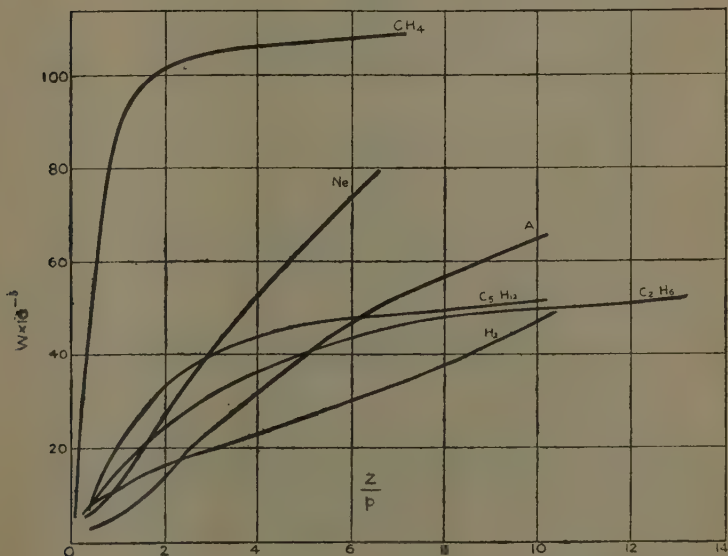


Fig. 3.



of given average velocity in its collisions with gaseous molecules of methane ; it is given by the equation

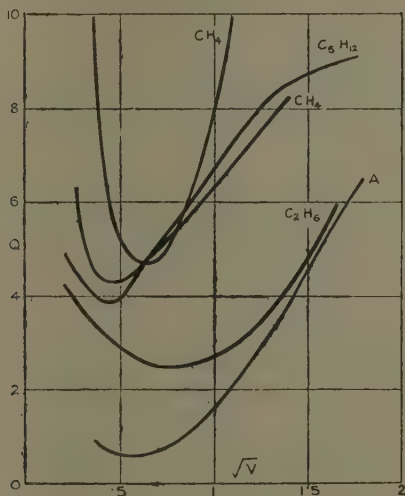
$$\lambda = 2.46 \frac{W^2}{U^2}.$$

TABLE II.

Z/p	k	k_{ex}	$U \times 10^{-6}$	$U_{ex} \times 10^{-6}$	$W \times 10^{-5}$	$L \times 10^2$	$L_{ex} \times 10^2$	\sqrt{V}	$\sqrt{V_{ex}}$	Q	Q_{ex}	$\lambda \times 10^4$
.05	2.3	2.3	17.3	17.3	6.6	16.1	16.1	.29	.29	6.2	6.2	36
.1	2.9	3.4	19.5	21.1	15.0	20.4	22.1	.33	.35	4.90	4.55	45
.2	3.6	4.6	21.7	24.5	27.0	20.5	23.2	.36	.41	4.88	4.31	381
.4	4.5	5.8	24.2	27.5	48.5	20.5	23.4	.40	.46	4.88	4.27	988
.6	5.7	7.1	27.3	30.5	65.0	20.7	23.1	.46	.51	4.83	4.33	1394
.8	7.6	8.6	28.8	33.5	76.0	21.0	22.3	.48	.56	4.76	4.48	1713
1.0	9.3	10.2	34.9	36.5	83.0	20.9	21.9	.58	.61	4.78	4.57	1392
1.5	14.0	15.0	42.8	44.3	94.0	18.8	19.4	.71	.74	5.32	5.16	1187
2.0	18.9	20.0	49.7	51.1	101.5	17.7	18.2	.83	.85	5.65	5.50	1025
3.0	29.0	30.5	61.6	63.1	106.0	15.2	15.6	1.03	1.05	6.58	6.41	728
4.0	39.1	41.5	71.5	73.7	107.5	13.4	13.9	1.19	1.23	7.46	7.19	556
5.0	48.6	52.2	79.7	82.6	108.0	12.0	12.4	1.33	1.38	8.33	8.07	452
6.0	58.5	63.0	87.5	90.7	108.3	11.0	11.5	1.46	1.51	9.09	8.70	378
7.0	67.2	73.5	93.7	98.0	108.5	10.2	10.6	1.56	1.63	9.80	9.43	330
8.0	74.0	83.0	98.4	104.2	108.8	9.4	9.9	1.64	1.74	10.64	10.10	301

In fig. 4 the effective cross-section of methane molecules with respect to slow electrons is plotted against the velocity of the electrons expressed in terms of $\sqrt{\text{volts}}$; the corresponding curves are given for methane and argon, as obtained by Ramsauer and Kollath *, pentane (McGee and Jaeger) †, and argon (Townsend and Bailey).

Fig. 4.



An inspection of these curves reveals the following features :—

1. The curve here obtained for methane by the Townsend diffusion method is but little altered in shape and position by the greatest possible error in the values obtained for k owing to the formation of ions.

2. The curves obtained by Townsend's method exhibit less sharp minima than those obtained by Ramsauer's method. This characteristic difference, which applies equally well to the maxima, has been observed in all the

* C. Ramsauer and R. Kollath, *Ann. d. Phys.* xii. pp. 529 & 837 (1932).

† J. D. McGee and J. C. Jaeger, *Phil. Mag.* vii. (Dec. 1928).

gases so far investigated *. This is to be expected from the statistical character of the calculations involved in the Townsend method.

3. The agreement in the minimum values obtained for the cross-section of methane molecules by the two different methods is very satisfactory. The minimum of Q for CH_4 is $4.7 \text{ cm.}^2/\text{cm.}^3$ at a velocity of $0.6 \sqrt{V}$ according to Ramsauer and Kollath, and is $4.76 \text{ cm.}^2/\text{cm.}^3$ at a velocity of $0.5 \sqrt{V}$ according to the present investigation by the Townsend method.

4. The $Q-\sqrt{V}$ curves of CH_4 and argon are approximately parallel to one another according to both methods.

The parallelism of the cross-section curves for methane and argon mentioned in 4 extends up to electron velocities of $5 \sqrt{\text{volts}}$, and has been interpreted by some experimenters † as indicating a close structural similarity between the methane molecule and the atoms of the inert gases. In support of this interpretation many other properties are quoted by Brüche in which methane resembles the inert gases.

Other experiments, made by Bullard and Massey ‡ and Arnot § on the angular scattering of electrons by gas molecules have also shown that the variation of angular scattering with velocity has qualitatively the same cause for methane and argon for electrons whose velocities range between 4 and 30 volts. Arnot explains the agreement on the assumption that the four electrons in the L-shell of the carbon atoms and the four electrons of the four hydrogen atoms combine to form a closed 8-shell in the same way as do the eight M-electrons of argon. The variations in the cross-section and angular scattering for electrons of low velocity (< 30 volts) are then considered to be determined solely by this closed 8-shell, the nuclei and inner shells first becoming of importance for electrons of velocity greater than 30 volts. There seems little justification for making such deductions concerning molecular structure from a mere similarity in the shape of the cross-section curves, which may in some circum-

* Cf. Brose and Saayman, *loc. cit.*

† *Vide, e. g., E. Brüche, Ergebnisse der exakten Naturwissenschaften*, viii. p. 185.

‡ Bullard and Massey, *Proc. Roy. Soc. cxxxiii. A*, p. 637 (1931).

§ Arnot, *Proc. Roy. Soc. cxxxiii A*, p. 615 (1931).

stances be regarded as fortuitous *. It must be regarded as an advantage of the Townsend method that besides allowing the $Q-\sqrt{V}$ curves to be determined it also allows the $\lambda-\sqrt{V}$ curves to be obtained, which give additional information on the interactions involved in the collisions between the slow electrons and the gas atoms or molecules. If the processes of interaction of slow electrons with methane molecules and argon atoms were completely analogous it would be reasonable to expect the average amounts of energy lost by the electrons in such processes to be of the same order of magnitude and to vary in the same way with the velocity in both gases—that is, the $\lambda-\sqrt{V}$ curves should be similar in character. It is found, however, that of all gases investigated up to the present time there are no two whose $\lambda-\sqrt{V}$ curves show a greater dissimilarity than those of CH_4 and argon. The measure of this disagreement may be seen in fig. 5, in which the λ -values for argon on this scale are so small that its $\lambda-\sqrt{V}$ curve is indistinguishable from the $\lambda=0$ axis. Methane yields the highest and argon the lowest λ -values so far measured; the average fraction of the energy lost by an electron in a collision with a methane molecule is several thousand times as great as in a collision at the same velocity with an argon atom. Moreover, in the case of methane and pentane, gases whose molecules are known to have similar structures, the $\lambda-\sqrt{V}$ curves are of similar form.

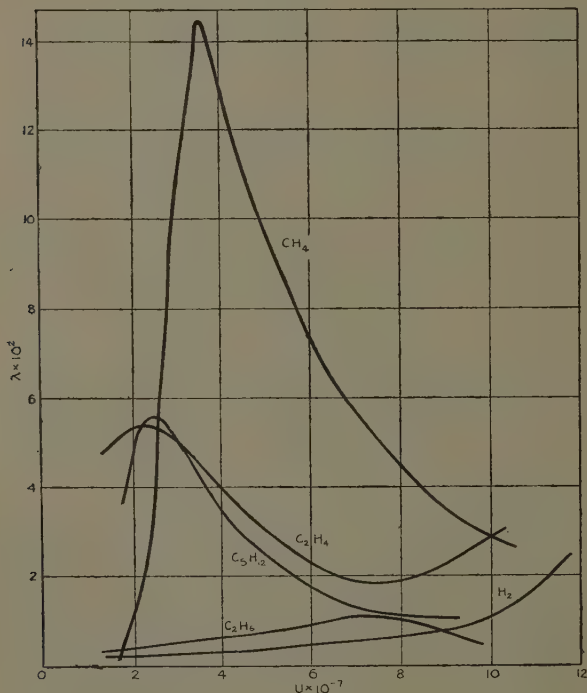
Bailey † has pointed out that there is a connexion between the shape of the $\lambda-\sqrt{V}$ curve of a gas and the position of its infra-red absorption bands. He finds that for many gases the value of \sqrt{V} or V at which λ , the average loss of energy, exhibits a maximum corresponds fairly closely with the wave-length which marks the position of one of the main infra-red absorption bands of the gas (where the well-known relationship wave-length \times volt velocity = 12340 is used). The main infra-red absorption bands of methane are indicated in fig. 5, where it is clearly seen that they fall well within the region in which λ has its maximum values. We thus see a further difference between the behaviour of methane molecules and the atoms of the inert gases; methane possesses

* H. L. Brose and J. E. Keyston, 'Nature,' Nov. 22, 1931.

† V. A. Bailey, *Phil. Mag.* xiii. p. 993 (May 1932).

strong infra-red absorption bands, whereas the inert gases are completely transparent in this region. We may say that methane and similar molecules have the property of selective absorption for slow electrons in addition to the general diffraction properties possessed by the atoms of the inert gases. The similarity in the cross-section

Fig. 5.



curves of methane and argon must be regarded as accidental, and the only legitimate conclusion to be drawn from this similarity alone (that is, without regard to the $\lambda - \sqrt{V}$ curves of these gases) is that the methane molecule and the argon atom both possess a high degree of symmetry and have fields of force whose boundaries have approximately equal degrees of sharpness, a conclusion which may be confirmed by theoretical investigation.

LXXII. *X-ray Studies on the Systems Tin-Antimony and Tin-Arsenic.* By G. HÄGG and A. G. HYBINETTE *.

X-RAY studies on the binary systems Sn-Sb and Sn-As have been reported in this Journal by Bowen and Morris Jones †, and by Willott and Evans ‡ respectively. According to these reports some phases in the two systems show variations in the volume of the unit cell with the composition, which are not compatible with the known relative atomic dimensions of the components, assuming solid solutions of the substitution type. If these observations were true, one must accept either rather unusual atomic dimensions or solid solutions of the interstitial type. As this type of solid solution is rare among inter-metallic phases, it seemed worth while to repeat the studies of the systems mentioned. The results obtained differ so much from the results of the earlier investigations that a rather detailed report is made necessary.

THE SYSTEM SN-SB.

The above-mentioned study by Bowen and Morris Jones, as well as the works carried out by Williams §, Broniewski and Sliowski ||, and Iwasê, Aoki, and Ôsawa ¶ agree in the fact that at room-temperature there exists only one intermediary phase in the system Sn-Sb. This phase has an extended homogeneity range which includes the composition with 50 atomic per cent. Sb. Since the X-ray studies by Goldschmidt *, Ôsawa †, as well as Bowen and Morris Jones, indicated a structure of the NaCl type for this phase, it could be assumed that the formula SnSb would correspond to the most characteristic composition of this phase. In the following, this phase is referred to as the SnSb phase.

* Communicated by the Authors.

† E. G. Bowen and W. Morris Jones, *Phil. Mag.* xii. p. 441 (1931).

‡ W. H. Willott and E. J. Evans, *Phil. Mag.* xviii. p. 114 (1934).

§ R. S. Williams, *Zeitschr. anorg. Chem.* lv. p. 1 (1907).

|| W. Broniewski and L. Sliowski, *Comptes Rendus*, clxxxvi. p. 1615 (1928).

¶ K. Iwasê, N. Aoki, and A. Osawa, *Sc. Rep. Tôhoku Imp. Univ.* xx p. 353 (1931).

* V. M. Goldschmidt, *Geochemische Verteilungsgesetze*, viii. (1927).

† A. Osawa, 'Nature,' cxxiv. p. 14 (1929).

Phil. Mag. S. 7. Vol. 20. No. 136. *Suppl. Nov.* 1935. 3 O

Preparation of Alloys and Experimental Methods.

The alloys were prepared from Kahlbaum's purest tin and antimony by melting these metals together in evacuated and sealed pyrex tubes. The amounts of the components were weighed, and as the method prevented all losses, analyses seemed unnecessary.

A total of seventeen preparations were made. After melting, the tubes with the ingots were annealed 120 hours at 400° C., 42 hours at 300° C., and 215 hours at 200° C. For the X-ray study these samples were powdered and the powders recrystallized at 200° C. The powder photograms were obtained in focussing cameras, using CrK-radiation.

The Sn Phase.

The earlier studies on the Sn-Sb system indicate a solubility of Sb in the Sn phase of about 10 atomic per cent. of Sb. X-ray measurements on this solid solution have only been performed by Bowen and Morris Jones. The length of the axis a of the tetragonal cell of pure Sn was found to be 5.818 Å. and the axial ratio $c/a=0.546$. The addition of up to 9 per cent. of antimony caused an expansion of the a axis to $a=5.836$ Å., with no change of the axial ratio. Further addition of Sb caused no change in these dimensions, and, as a consequence, Sn seemed to dissolve up to 9 per cent. Sb at about 200° C.

The results of the present study are rather similar. The axial lengths of pure Sn were $a=5.819$ Å. and $c=3.174$ Å. ($c/a=0.5455$). From the variation of the dimensions with the composition, the homogeneity limit richest in Sb seems to lie at about 9 atomic per cent. Sb, and here the dimensions were $a=5.834$ Å. and $c=3.174$ Å. ($c/a=0.5441$).

Determinations of the specific gravities of the preparations within the homogeneity range of the Sn phase indicate that the solution is of the substitution type. Consequently, the increase in dimensions with rising amount of Sb agrees with the generally accepted fact that Sb atoms are larger than Sn atoms.

The SnSb Phase.

According to Williams, the homogeneity range of this phase lies between 49.8 and 52.8 atomic per cent. Sb at

200° C. Broniewski and Sliwowski found the corresponding limits to be 40 and 54 atomic per cent., Iwasê, Aoki, and Ôsawa 43 and 58 atomic per cent., and Bowen and Morris Jones 40 and 54 atomic per cent.

The first X-ray measurements on this phase were carried out by Goldschmidt, who reports a NaCl structure with a length of the cube edge of $a=6.13$ Å. The Japanese authors are of the opinion that SnSb crystallizes in a simple cubic lattice with a cube edge of about half the length of that reported by Goldschmidt. They have evidently overlooked the fact that the interferences from a NaCl lattice built up from Sn and Sb atoms must correspond to a simple cubic lattice owing to the similar scattering factors of Sn and Sb. The cube edge corresponding to the NaCl cell will be 6.104 Å. at 43 per cent., 6.122 Å. at 50 per cent., and 6.108 Å. at 55 per cent. Sb. The dimensions show, consequently, a maximum at 50 per cent. Sb, but, as will be seen later, this is probably due to heterogeneities.

Bowen and Morris Jones report a NaCl structure and found the dimensions to decrease with increasing Sb content. At 40, 50, and 54 atomic per cent. Sb they measured the cube edges, finding 6.126, 6.120, and 6.110 Å. respectively. Since the extension of the homogeneity range is most probably due to a substitution of atoms, and Sb atoms are known to be larger than Sn atoms, the decrease in dimensions with increasing Sb content is very strange. As an explanation, Bowen and Morris Jones suggest that the SnSb phase is constituted by positive Sn ions and negative Sb ions, but such an ionic constitution seems very unlikely.

An inspection of the ingots with an Sb content of about 50 atomic per cent. showed that the crystals of the SnSb phase hardly could be cubic. After the long annealing the ingots consisted only of a few large crystals. These crystals showed mainly one extremely pronounced cleavage plane, a fact which cannot be connected with cubic symmetry. In accordance with that, the powder photograms never indicated a cubic NaCl structure. Most of the lines corresponding to a NaCl structure are split up into two or more lines, indicating a distortion of the cubic lattice. In fact, the photograms could be interpreted if a rhombohedral lattice was accepted. In Table I. the α lines from a photogram of a preparation with 52.4

atomic per cent. Sb. are listed. The rhombohedral indices and the calculated $\sin^2 \theta$ values correspond to a rhombohedron with a length of the rhombohedral edge $r=6.124 \text{ \AA.}$ and a rhombohedral angle $\alpha=89^\circ.38$. The calculated intensity values are based on the assumption that the rhombohedral structure is to be viewed as a distorted NaCl structure. The agreement between observed and calculated values is very good.

The above rhombohedral cell contains eight atoms. A smaller cell containing only two atoms can also be used

TABLE I.
 α -Lines in Powder Photographs of an Alloy with
52.4 atomic per cent. Sb.

Intensity.		Σh^2 in NaCl structure.	Rhombo- hedral indices.	$\sin^2 \theta$.	
Obs.	Calc.			Obs.	Calc.
v. st.	224	4	020	0.1380	0.1394
st.	74	8	{ 022	0.2755	0.2757
st.	74		{ 220	0.2823	0.2819
w.+	13	12	{ 222	0.4095	0.4090
st.	40		{ 222	0.4219	0.4213
m.+	27	16	040	0.5570	0.5576
st.	48	20	{ 402	0.6891	0.6908
st.	48		{ 420	0.7027	0.7032
m.	24	24	{ 242	0.8206	0.8210
st.	48		{ 242	0.8383	0.8395
m.	24		{ 242	0.8456	0.8456

for the description of the structure, but the above is chosen because it better shows the relation between this structure and the undeformed NaCl structure.

Studies on other alloys containing the SnSb phase showed that it is always rhombohedral at ordinary temperatures and never represents an undeformed NaCl structure. The unit dimensions and the degree of deformation vary with the composition. However, in spite of the very careful heat treatments it was found that heterogeneities made it impossible to plot the dimensions as functions of the compositions. Remeltings and new heat treatments also showed the difficulty in obtaining defined properties at a given composition. The heterogeneities are probably partially connected with the trans-

formation of the SnSb phase at 320° C., mentioned below, and might also be due to the peritectic nature of the high temperature modification, stable above this temperature.

We are of the opinion that the disagreements between the results of previous investigators and the unlikely variation in the dimensions found by Bowen and Morris Jones are mainly caused by heterogeneities of the alloys studied. The way in which the lines of the rhombohedral phase are interpreted as lines of a supposed cubic structure may also give rise to irregularities.

Judging from the presence of lines of the Sn phase it seems as if the limit of the homogeneity range of the SnSb phase richest in Sn lies at about 45 atomic per cent. Sb. The dimensions of the rhombohedral cell at this limit have been found to be $r=6.117 \text{ \AA.}$ and $\alpha=89^{\circ}70$. The volume of the rhombohedron is 228.9 \AA.^3 . This rhombohedron corresponds to a hexagonal cell containing 24 atoms, and with the axial lengths $a=8.629 \text{ \AA.}$ and $c=10.650 \text{ \AA.}$

With rising Sb content, r increases and α decreases, that is, the deformation of the cubic lattice increases. These changes correspond to a decrease of the axis a and an increase of the axis c in the hexagonal cell and cause a swelling of the lattice. As has been said, it was not possible to study these variations of the dimensions with composition in detail within the homogeneity range. From the appearance of lines belonging to the Sb phase we conclude that the Sb-saturation limit must be situated at about 55 atomic per cent. Sb. At this limit the dimensions of the rhombohedron are $r=6.138 \text{ \AA.}$ and $\alpha=89^{\circ}18$, and the volume of the rhombohedron $=231.2 \text{ \AA.}^3$. The corresponding hexagonal cell has the axial lengths $a=8.615 \text{ \AA.}$ and $c=10.790 \text{ \AA.}$

The above results show that the unit volume of the SnSb phase rises with increasing Sb content. This is in agreement with the facts that the solid solution is of the substitution type and that Sb atoms are larger than Sn atoms. The rise in volume when passing from the limit richest in Sn to the limit richest in Sb indicates a width of the homogeneity range of about 10 atomic per cent. This value is in accordance with the assumed positions of the limits at 45 and 55 atomic per cent.

It has been shown by Iwasê, Aoki, and Ôsawa that the SnSb phase undergoes a transformation at 320° C. These authors did not succeed in the determination of the

structure existing above this temperature. We have tried to prevent the transformation into the rhombohedral structure by quenching alloys from 350°C. , but the photograms only showed the presence of the rhombohedral phase. Evidently photograms must be taken at elevated temperatures to determine the nature of the high temperature phase. Since the Japanese authors could not detect any traces of the high temperature phase by microscopical examinations of quenched specimens, it is very likely that the two phases have similar structures. It might be that the atoms of the two phases are distributed over the same positions, but that the distribution is a more disordered one in the case of the high temperature phase. Another possibility might be that the high temperature phase represents an undeformed NaCl structure.

The Sb Phase.

Most authors agree in the opinion that Sb can dissolve about 10 atomic per cent. Sn. For pure Sb, Bowen and Morris Jones determined the dimensions of the rhombohedral cell, containing 4 atoms, as $r=6.220\text{ \AA.}$ and $\alpha=87^{\circ}40$. At 90 atomic per cent. Sb, corresponding to the homogeneity limit richest in Sn, the dimensions were $r=6.220\text{ \AA.}$ and $\alpha=86^{\circ}50$.

For the smallest rhombohedral cell, (containing 2 atoms) of pure Sb, we found the values $r=4.496\text{ \AA.}$ and $\alpha=57^{\circ}12$. The volume of this rhombohedron will be 60.04 \AA.^3 . The large rhombohedron will then have $r=6.221\text{ \AA.}$ and $\alpha=87^{\circ}42$, in close agreement with the values found by Bowen and Morris Jones.

With increasing Sn content the unit volume decreases, owing to the replacement of Sb atoms by small Sn atoms. The variation of the volume with the composition indicates that the homogeneity limit richest in Sn lies at 90–91 atomic per cent. Sb. Here the small rhombohedron shows $r=4.531\text{ \AA.}$, $\alpha=55^{\circ}96$, and the volume 59.63 \AA.^3 . The size of the corresponding large rhombohedron will be determined by the values $r=6.214\text{ \AA.}$ and $\alpha=86^{\circ}36$.

THE SYSTEM SN-AS.

The most accurate thermal and micrographic study of this system has been made by Mansuri*, who proposed

* Q. A. Mansuri, J. Chem. Soc. cxiii. p. 214 (1923).

an equilibrium diagram, which in all essential parts has been verified by the present investigation. Mansuri could not detect any solubility of As in Sn. He found two intermediary phases, Sn_3As_2 and SnAs . The former phase seemed to exist only at 40 atomic per cent. As, while the homogeneity range of the latter seemed to extend from 50 to 58 atomic per cent. As. The As phase was found to exist from 79 to 100 atomic per cent. As.

The results of the X-ray study on this system, carried out by Willott and Evans, deviate in many respects from Mansuri's equilibrium diagram. Willott and Evans found that Sn dissolved up to 40 atomic per cent. As, and, consequently, did not find any phase Sn_3As_2 at this composition. The only intermediary phase reported by Willott and Evans had a NaCl structure and was said to be homogeneous between 45 and 60 atomic per cent. As. The solubility of Sn in As agreed with the diagram of Mansuri.

Preparation and Analysis of Alloys. *Experimental Methods.*

Thirteen alloys ranging from 7.4 to 70.9 atomic per cent. As were investigated. They were prepared by heating the constituents (Kahlbaum's purest preparations) in sealed and evacuated pyrex tubes at 650° C. The powder photograms were obtained from powdered samples, recrystallized at 200° C.

For determination of the arsenic content of the alloys an amount containing about 20 mg. As was dissolved in concentrated H_2SO_4 in a distilling flask. About 5 g. FeSO_4 , 75 c.c. concentrated HCl , and some KBr were added to the solution. Then the flask was heated, and the AsCl_3 vapours developed were cooled and absorbed in a vessel containing 150 c.c. water. The transport of the AsCl_3 was accelerated by means of a stream of CO_2 , which was led through the apparatus during the distillation. When all AsCl_3 had been transferred to the absorption vessel, its amount was determined by titration with KBrO_3 , methyl orange being used as an oxidation indicator.

The specific gravity of several alloys was determined by weighing the powder in air and in benzene, according to a method which has been previously described*.

* G. Hägg, *Zeitschr. f. Krist.* lxxiv. p. 95 (1930)

All powder photograms were obtained in focussing cameras, using Cr K-radiation.

The Sn Phase.

As has already been mentioned, Willott and Evans were of the opinion that Sn can dissolve up to 40 atomic per cent. As. They report a considerable increase in the unit dimensions of the Sn phase with increasing As concentration. This fact is very astonishing, as As atoms are known to be considerably smaller than Sn atoms. Furthermore, the difference in size between the two components is not so large that an addition of the dissolved As atoms in the interstices of the Sn lattice is possible.

Our results are in contradiction to the interpretation of Willott and Evans and favour the view of Mansuri that As is not soluble in Sn. In all photograms of preparations with As contents between 0 and 40 atomic per cent. As, the lines of the Sn phase occupy exactly the same positions. The solubility of As in Sn must, therefore, be very small.

In the region up to 40 atomic per cent. As, where Willott and Evans report a homogeneous Sn phase, the present study shows the existence of two phases, the Sn phase and a second phase, which has been proved to be Sn_3As_2 .

According to the tables given by Willott and Evans their photograms evidently contain the lines of Sn_3As_2 , but they have been misinterpreted as belonging to a Sn phase with large dimensions.

The Phase Sn_3As_2 .

A preparation containing 34.1 atomic per cent. As showed lines of a new phase together with very faint Sn lines. The lines of the new phase occur alone in photograms from a preparation with 40.0 atomic per cent. As, while photograms of a preparation with 42.7 atomic per cent. As also show lines belonging to the next intermediary phase, SnAs . As a consequence, the new phase must be homogeneous at a composition close to 40 atomic per cent. As, and the formula Sn_3As_2 proposed by Mansuri seems very probable. The position of the lines was the same in all photograms, showing that the homogeneity range must

be very small. The α interferences of Sn_3As_2 are listed in Table II.

It was found that the strong lines of the powder photograph could be interpreted by means of a rhombohedral

TABLE II.

α Lines in Powder Photographs of Sn_3As_2 .

Intensity. Obs.	Rhombohedral indices.		$\sin^2 \theta$.	
	Small cell.	Real cell.	Obs.	Calc.
v.w.	..	011	0.1075	0.1086
w. +	..	122	0.1288	0.1298
w. +	..	444	0.1442	0.1452
st.	010	232	0.1527	0.1540
(v.w.)	..	233	0.1682	0.1691
(v.w.)	..	343	0.2051	0.2055
v.w.	..	344	0.2264	0.2266
st.	011	455	0.3023	0.3023
st.	$\bar{1}10$	$\bar{1}10$	0.3138	0.3137
(v.w.)	..	666	0.3274	0.3268
v.w.	..	565	0.3633	0.3628
v.w.	..	243, 566	0.3961	0.3954 0.3961
m.	111	777	0.4443	0.4448
w.	..	354	0.4587	0.4589
st.	$\bar{1}11$	133, 676	0.4680	0.4677 0.4687
v.w.	..	888	0.5803	0.5809
st.	020	464	0.6160	0.6160
w.	..	788, 576	0.6382	0.6381 0.6405
st.	021	032, 687	0.7585	0.7573 0.7585
st.	$\bar{1}20$	142, 577	0.7815	0.7815 0.7824
w.	..	899	0.7860	0.7864
m.	121	798, 9 10 9	0.8953	0.8946 0.8953
w.	..	10 10 10	0.9078	0.9077
m.	$\bar{1}21$	365	0.9295	0.9298
m.	$\bar{2}11$	$\bar{2}11$	0.9412	0.9412
w.	..	{ 122, 030 797, 9 10 10 }	0.9523	{ 0.9503 0.9503 0.9518 0.9527 }

cell with $r=2.914 \text{ \AA.}$ and $\alpha=88^\circ 90$. The corresponding hexagonal cell has the axes $a=4.082 \text{ \AA.}$ and $c=5.142 \text{ \AA.}$ The rhombohedron, which can be regarded as a slightly distorted cube, has the volume 24.73 \AA.^3 As the observed density of Sn_3As_2 is 6.69, this rhombohedron must contain only one atom, which gives a theoretical density of 6.752.

The atoms are evidently distributed among the positions of a simple, approximately-cubic lattice, but the weak lines of the photogram indicate that the real unit cell must be larger than the small rhombohedron mentioned above. The dimensions of the real unit cell were determined by means of Laue and rotation photograms of a small crystal fragment of Sn_3As_2 . The alloy in question was composed of a few very large crystals possessing one very pronounced plane of cleavage. As the crystals were very soft, it was impossible to split off a crystal fragment without deformation, but the lattice was successfully corrected by pressing the fragment between two glass plates.

The Laue photograms showed that the trigonal axis of the rhombohedron was at right angles to the cleavage plane. The Laue symmetry was D_{3d} . Rotation photograms were obtained with the crystal rotating around the trigonal axis, around one digonal axis, and around a direction at right angles to the two former. It was found that the real unit cell is a rhombohedron with $r=12.23 \text{ \AA.}$ and $\alpha=19^\circ 22'$. This corresponds to a hexagonal cell with the same a axis, but with a c axis seven times as long as in the above mentioned small hexagonal cell. The real rhombohedral unit cell has a volume of 173.12 \AA.^3 , that is, seven times as large as the volume of the small one. Consequently, it must contain seven atoms.

It is astonishing to find a cell content of seven atoms for a phase with the composition Sn_3As_2 . As has already been mentioned, an alloy with 42.7 atomic per cent. is not homogeneous, and this fact, together with Mansuri's results, shows that the phase is not homogeneous at the composition Sn_4As_3 (42.9 atomic per cent. As), which would have been in accordance with a number of seven atoms per unit cell. One has then to consider mainly three different cases :—(1) The real cell is larger than the rhombohedron, containing seven atoms ; (2) the atoms are distributed at random among the positions of the rhombohedral lattice ; (3) the structure corresponds to an ideal formula of Sn_4As_3 , but the phase is only homogeneous if some As atoms have been replaced by Sn atoms.

There is no experimental evidence of case (1), and it seems not possible to obtain correct relative intensities in

case (2). Case (3) is then left, and this possibility seems to be supported by some observations made by Vivian in the system SnP *. This system contains one intermediary phase which at room-temperature is homogeneous between the limits Sn_3P_2 and Sn_4P_3 , and whose microstructure is extremely similar to the microstructure of Sn_3As_2 observed by Mansuri and by us. We are of the opinion that Sn_3As_2 and Sn_3P_2 are isomorphous and that both are to be regarded as solutions of Sn in a structure of the composition Sn_4X_3 , but that this composition represents a stable phase only in the SnP system.

The determination of the structure of Sn_3As_2 must be carried out in the way that four Sn atoms and three As atoms must be placed in the rhombohedron containing seven atoms so that the positions together form an approximately cubic lattice. Then some of the As atoms must be replaced by Sn atoms.

Of the rhombohedral space groups with the Laue symmetry D_{3d} , the groups C_{3v}^6 and D_{3d}^6 are not in accordance with the observed interferences. The groups C_{3v}^5 , D_3^7 , and D_{3d}^5 are then the only possible ones. In order to obtain a grouping approaching a simple cubic lattice, the atoms must all be situated on the trigonal axis of the rhombohedron. The highest symmetry of such a grouping will be possible in D_{3d}^5 . The atoms must be placed on the trigonal axis at intervals of about $1/7$ of the length of this axis. If one As atom is placed in 000 the other atoms must be situated in three twofold positions uuu , $\bar{u}\bar{u}\bar{u}$, and in order that the distances between the atoms should be about $1/7$ of the length of the trigonal axis, u must have values of about $1/7$, $2/7$, and $3/7$. The coordinates of the seven positions and the three possibilities for the distribution of the atoms among these positions will be the following :—

	1.	2.	3.
000	1 As	1 As	1 As
$1/7 \ 1/7 \ 1/7, \ 6/7 \ 6/7 \ 6/7$	2 Sn	2 Sn	2 As
$2/7 \ 2/7 \ 2/7, \ 5/7 \ 5/7 \ 5/7$	2 As	2 Sn	2 Sn
$3/7 \ 3/7 \ 3/7, \ 4/7 \ 4/7 \ 4/7$	2 Sn	2 As	2 Sn.

It was assumed that As atoms were replaced at random by Sn atoms so as to attain the composition Sn_3As_2 . The

* A. C. Vivian, J. Inst. Metals, xxiii. p. 325 (1920).

TABLE III.
Observed and Calculated Intensities for Sn_3As_2 .

<i>hkl.</i>	Intensity.		<i>hkl.</i>	Intensity.		Intensity.	
	Obs.	Calc.		Obs.	Calc.	Obs.	Calc.
011	v.w.	18	777	m.	44	032	1.7
121	0	0.98	354	w.	2.9	687	179
122	w. +	14	133	st.	129	142	177
444	w. +	3.9	676	0	1.4	577	0.87
232	st.	670	242	0	0.17	899	0.87
233	(v.w.)	1.2	677	0	0.16	143	0.22
343	(v.w.)	0.42	244	0	0.08	686	0.11
344	v.w.	0.34	353	0	0.07	253	0.11
555	0	0.23	645	0	0.29	254	0.11
454	0	0.49	888	v.w.	0.02	798	0.11
455	st.	239	355	0	0.13	9 10 9	82
110	st.	224	787	0	0.14	364	0.22
021	0	0.35	464	st.	102	688	0.11
666	(v.w.)	0.05	788	0	1.0	10 10 10	0.29
132	0	0.61	576	w.	0.13	365	158
565	v.w.	2.2	466	0	0.94	211	79
243	v.w.	3.8	575	0	0.06	122	0.05
566		0.12	120	0	0.23	030	0.05
111	0	0.22	898	0	0.05	797	0.81
020	0	1.6	999	0	0.04	9 10 10	0.10
022	0	0.10	121	0	1.8		
131	0	1.5	031	0	0.11		

intensities calculated under this assumption for the three cases show that case (2) best corresponds to the observed intensities. A comparison between intensities observed and calculated for case (2) is given in Table III. The agreement is fairly good, but it can be seen that the basal plane gives reflexions which are stronger than could be expected from the calculated intensity values. It could be shown that this is due to absorption and orientation effects caused by the pronounced laminar shape of the grains of the crystal powder. This effect makes a more exact determination of the parameters difficult. Variations of the values have been tried, but as the best results have been obtained with the values $1/7$, $2/7$, and $3/7$ they have been accepted for the present. A control of the structure proposed here, for example through a study of Sn_3P_2 and Sn_4P_3 , is very desirable.

In the Sn_3As_2 structure every atom is surrounded by six atoms, forming a nearly regular octahedron, and at equal distances of 2.91 \AA . The unit rhombohedron and the immediate surroundings of a trigonal axis of the ideal structure, corresponding to the composition Sn_4As_3 , are shown in fig. 1. In this ideal structure 2 Sn atoms are surrounded by 6 As atoms, 2 Sn atoms by 3 Sn + 3 As atoms, and 3 As atoms by 6 Sn atoms.

The SnAs Phase.

According to Mansuri, this phase is homogeneous between 50 and 58 atomic per cent. As. At 50 atomic per cent. Goldschmidt* found a NaCl structure with a lattice constant of $a=5.70_8 \text{ \AA}$. Willott and Evans confirmed this structure and reported a homogeneity range of the phase extending from 45 to 60 atomic per cent. As. They found a lattice constant of $a=5.71_4 \text{ \AA}$. at 45 and $a=5.71_7 \text{ \AA}$. at 60 atomic per cent., while the constant at 50 atomic per cent. showed a minimum value of 5.68_1 \AA .

The present investigation showed no signs of a variation of the lattice constant. In all alloys, a value of $a=5.716 \text{ \AA}$. was obtained, indicating that the homogeneity range must be very small. Alloys with 45.8 atomic per cent. As and less showed lines of SnAs and Sn_3As_2 , while alloys with 52.4 atomic per cent. and more showed lines of SnAs and of the As phase. One has, therefore,

* V. M. Goldschmidt, Trans. Faraday Soc. xxv. p. 253 (1929).

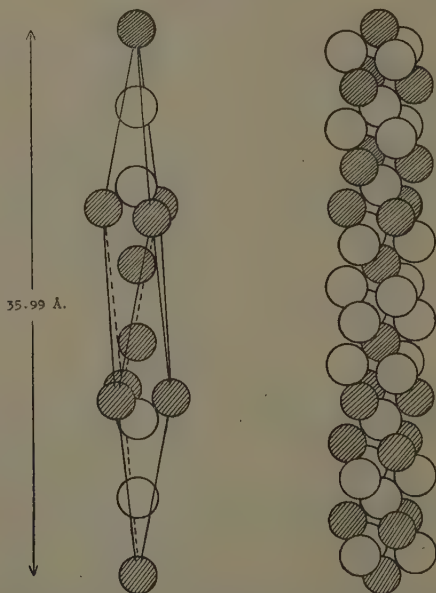
reason to assume a narrow homogeneity range close to the composition SnAs .

In the case of a NaCl structure the value $a = 5.716 \text{ \AA}$. corresponds to a theoretical density of 6.845, which is identical with the observed value.

The As Phase.

For pure As Willott and Evans determined the constants of the rhombohedron containing four atoms to be

Fig. 1.



Structure of Sn_3As_2 corresponding to the ideal composition at 42.9 atomic per cent. As. Left: unit rhombohedron. Right: immediate surroundings of a trigonal axis. As atoms shaded.

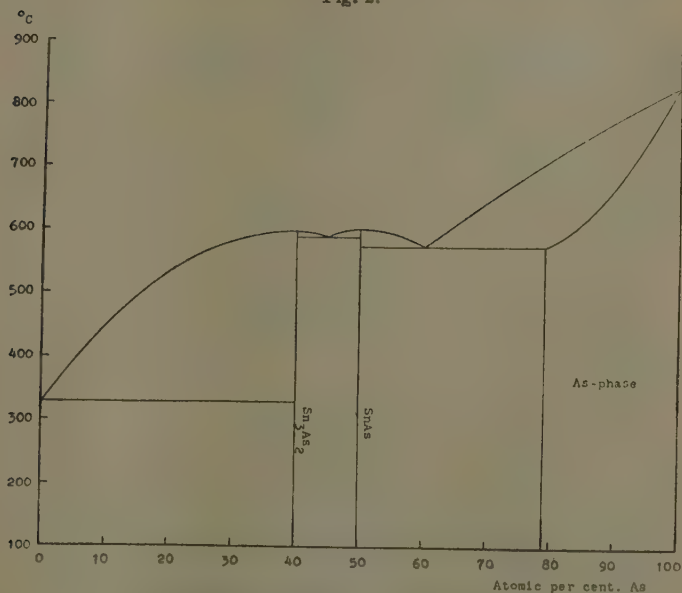
$r = 5.59_0 \text{ \AA}$. and $\alpha = 84^\circ 60$. They found the homogeneity range of the As phase to extend to 79 atomic per cent. As, and at this limit the constants were $r = 5.59_1 \text{ \AA}$. and $\alpha = 85^\circ 00$.

We found the constants of the small rhombohedron (containing 2 atoms) of pure As to be $r = 4.123 \text{ \AA}$. and

$\alpha=54^{\circ}10$. The volume of this rhombohedron is $42\cdot73 \text{ \AA}^3$. The constants of the corresponding large rhombohedron will be $r=5\cdot573 \text{ \AA}$. and $\alpha=84^{\circ}62$.

The constants of the As phase, saturated with Sn, were determined in a preparation with 70·9 atomic per cent. As; for the small rhombohedron $r=4\cdot224 \text{ \AA}$., $\alpha=52^{\circ}80$, and the volume $44\cdot29 \text{ \AA}^3$; for the corresponding large rhombohedron $r=5\cdot652 \text{ \AA}$., and $\alpha=83^{\circ}32$. The increase in volume is in good accordance with a solubility limit

Fig. 2.



Equilibrium diagram of the system Sn-As.

at about 79 atomic per cent. As. Contrary to Willott and Evans these measurements show that the dissolved Sn causes a marked increase in r and a diminution of the rhombohedral angle.

The Equilibrium Diagram.

In fig. 2 is given an equilibrium diagram of the system SnAs, which is in accordance with the results of the present

investigation. It differs only from Mansuri's diagram in the respect that the SnAs phase here has been drawn without any extended homogeneity range.

Summary.

In the systems Sn-Sb and Sn-As the structures and homogeneity ranges of the different phases have been studied by means of X-rays. The following may be mentioned as the main new points among the results of this investigation:—

System Sn-Sb.—The phase existing at room-temperature around the composition SnSb has a homogeneity range between about 45 and 55 atomic per cent. Sb. At the limit richest in Sn it has a deformed NaCl structure. The unit cell is a rhombohedron with $r=6.117 \text{ \AA.}$, $\alpha=89^\circ.70$, and the volume 228.9 \AA.^3 . With increasing Sb content the volume and deformation of the unit cell increase, and at the limit richest in Sb the rhombohedron is characterized by $r=6.138 \text{ \AA.}$, $\alpha=89^\circ.18$, and the volume 231.2 \AA.^3 .

System Sn-As.—No solubility of As in the Sn phase could be detected.

Two intermediary phases have been found with very narrow homogeneity ranges at the compositions Sn_3As_2 and SnAs.

The Laue symmetry of Sn_3As_2 is D_{3d} , and its unit cell is a rhombohedron with $r=12.23 \text{ \AA.}$ and $\alpha=19^\circ.22$. This rhombohedron contains seven atoms which occupy positions nearly corresponding to a simple cubic lattice. The structure corresponds probably to an ideal formula of Sn_4As_3 , where some As atoms have been replaced by Sn atoms. The most probable space group is D_{3d}^5 . If 1 As is placed in 000, the other atoms occupy three two fold positions uuu , $\bar{u}\bar{u}\bar{u}$. At the ideal composition Sn_4As_3 , 2 Sn would occupy such a position with $u=1/7$, 2 Sn another with $u=2/7$, and 2 As a third with $u=3/7$. In the stable phase Sn_3As_2 , As atoms in this structure are probably replaced at random by Sn atoms so as to give the formula Sn_3As_2 .

The phase SnAs has a NaCl structure with the lattice constant 5.716 \AA. No variation of this constant with the composition has been found and, consequently, the homogeneity range of this phase must be narrow.

Arsenic dissolves about 21 atomic per cent. Sn. The dissolved Sn causes an increase in the rhombohedral edge and a diminution of the rhombohedral angle of the As phase.

Institute of General and Inorganic Chemistry,
Metallographic Institute,
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May 1935.

LXXIII. *Recent Investigations on Electrets.* By A. GEMANT. (*Communicated from the Engineering Laboratory, Oxford University* *.)

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1. *Introduction.*

IN 1925 M. Eguchi ⁽¹⁾ published a paper dealing with permanently electrified bodies, so-called *electrets*. He described a method of producing such bodies, and stated that the charges obtained proved to be constant over a period of more than a year. Though this discovery was a really remarkable one, surprisingly few authors have dealt with the subject in the last decade ⁽²⁾. Mr. B. L. Goodlet suggested to me that it was worth proceeding further with the investigation. My stay at the Engineering Laboratory of the University of Oxford seemed to be a good opportunity to carry out this proposal.

Though the investigation is not complete, the material

* Communicated by Prof. R. V. Southwell, M.A., F.R.S.

seems sufficient to warrant publication. The purpose of the investigation was threefold :—

First it was necessary to prove whether the stated effects of Eguchi were really reproducible.

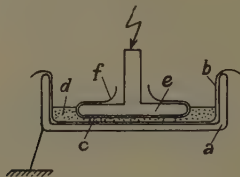
Secondly, the mechanism of the underlying physical process had to be clarified. Very little on this point has been done since Eguchi's paper appeared, so there is ample justification for this.

Thirdly, it was necessary to estimate the real significance of the electret. Is it really an important object, and, if so, why? There was also the question of the technical applications.

2. Verification of Eguchi's Work.

(a) *The Making of Electrets*.—The method adopted was similar to that described by Eguchi, though in some

Fig. 1.



Apparatus for making electrets.

respects simpler. The principle is to pour a suitable wax (for composition, see below) in the molten state into a condenser, apply a voltage, and let it solidify under the electric stress. The condenser is shown on fig. 1; *a* is a flat brass dish, covered on its inner surface with tin-foil (*b*). This is necessary in order to facilitate removal of the solid wax. The tin-foil must be thin and free from holes, and has to be pressed gently against the walls by means of a suitable cylinder, for instance a cork. The inner diameter of the dish was 4 cm.

To obtain a given spacing between the electrodes, three small pieces of ebonite (*c*) were placed in the melted wax (*d*). The spacing in our experiments was 1.6 mm. The upper electrode is a brass disk *e* (diameter = 2.5 cm.), with rounded edges. It has to be wrapped in tin-foil, *f*, in the same way as the dish.

The condenser is conveniently heated by means of a gas burner. The lower electrode may be earthed, the upper being connected to the high-voltage source. For producing the high continuous voltage, a set consisting of transformer, kenotron valve, and smoothing condenser was used. Voltage was measured by means of a liquid high-resistance potentiometer ⁽³⁾ and a static voltmeter for 450 volts. Usually 1800 volts were applied, corresponding to a field of 11 kv./cm.

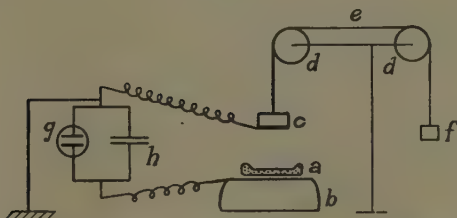
The starting temperature was about 100–120° C. The application of the electric field lasted one hour; this was enough to allow the specimen to cool down to room-temperature. In nearly all experiments earth was positive, and the upper high tension electrode negative.

Fig. 2.



Cross-section of electret.

Fig. 3.



Equipment for measuring the charge of electrets.

After removing the voltage the lower tin-foil was left on the specimen, but the upper tin-foil was taken off and replaced by a loose one, arranged to short the electret, and only removed for measuring or other purposes. The cross-section of a completed specimen is shown on fig. 2.

(b) *Measuring Equipment.*—The measuring equipment was also similar to that used by Eguchi (fig. 3). The electret *a* was placed on a metal sheet which rested on a paraffin block *b*. A small porcelain cylinder *c*, with metallized bottom, was situated above the electret.

It could be raised or lowered by means of the wheels d , the thread e , and the weight f .

The metal sheets on the paraffin block and on the porcelain cylinder were connected to a quadrant electrometer g in parallel with the condenser h . For convenience, the upper electrode was kept earthed, as its insulation was not so good as that of the lower one.

The quantity measured was the free surface charge of the electret; c was first lowered so as to touch the upper surface of a , while the electrometer was kept short-circuited. A charge opposite in sign to that on the upper surface of a was then induced on c . On releasing the short and lifting c , its charge passed over in the condenser h and caused a deflexion of the electrometer. Let s be the area of c , q the surface density of charge of the electret, V the voltage measured, K the joint capacity of h and g , then

$$q = \frac{KV}{s}.$$

In our special case s was 3 cm.², K 180 cm. Using the calibration value of the electrometer (37 cm. deflexion on the scale for 18 volts), and remembering that it is a quadratic instrument, we have

$$q = 0.6\sqrt{D} \text{ abs.,}$$

D denoting the deflexion in cm. By disconnecting the condenser h from the electrometer, the sensitivity could be raised 4.5 times. The total range for the specific charge covered was 0.2 to 6 abs. electrostatic units.

It proved to be very important to determine the sign of the charge measured. The procedure adopted was as follows. The electrometer was shorted, c lowered, and the short removed. Now the electrometer was charged usually to 18 volts by means of a battery, earth being positive. On lifting c , the deflexion of the electrometer either increased or decreased. In the first case the charge of c must be positive, indicating a negative charge of the upper electret surface. In the second case the same surface must be positive.

(c) *General Results.*—The method described above verified most of the statements of Eguchi; and also extended his observations on several points.

If prepared and preserved correctly, the electrets exhibit charges which have lasted with undiminished magnitude since May 1934 (see below). The charges observed attain a magnitude of five absolute units per cm.²

The application of a high field to dielectrics generally gives rise to accumulation of transient charges near the surfaces. As to the sign of these charges, the author has pointed out in several previous papers (^{3a}) that generally both kinds of charges may be observed in dielectrics. Similarly, we observe both kinds of charges on electrets. One has the opposite sign to that of the adjacent polarizing electrode, and for the sake of shortness will be denoted as *heterocharge*; the other has the same sign as the adjacent polarizing electrode, and will be denoted as *homocharge*.

Usually, but not always, a heterocharge prevails during the first few days after making; thereafter this charge falls to zero and becomes reversed. The final charge, which lasts a considerable time, is therefore usually a homocharge. Exceptions from this rule will be described later.

The homocharge is not superficial. Scraping the surface diminishes the charge temporarily, but in a few days the electrets recover from this manipulation. This confirms the conclusion already emphasized by Eguchi, namely, that the electrification is a volume effect.

3. Significance of the Electret.

The electret must be considered as the electrical analogue of a permanent magnetic shell. There is a general belief that such a thing is an impossibility, owing to the fact that free charge carriers will rapidly neutralize any electrified body. This is, however, not the case. Electrification by friction, of course, being a surface effect, cannot be of long duration. Electrification by applying high tension—as often observed with oils, for instance, in engineering—is also temporary. Even the charge of a piezo-crystal, though based on a volume effect, becomes quickly neutralized. But these electrets prove that the life of an electrification may be considerable. How this fact is consistent with the universal existence of free ions will be discussed in Section 5. Here we shall take the fact as given.

An electret is characterized by its specific surface charge q (or electric moment per unit volume). It seems important to emphasize that such notions as the potential of an electret have little meaning. The potential the charges assume is determined simply by the capacity of the system in which the field is produced. Consider fig. 2; the best way of producing a field is to raise the upper plate somewhat from the upper electret surface. The electric force is then $4\pi q$, and if the distance d is small the potential V becomes

$$V = 4\pi q \cdot d.$$

With increasing distance the potential grows, as is well known, more and more slowly, until it reaches a limiting value. It is therefore evident that no definite potential exists; the primary and characteristic quantity is the specific charge q . For a distance of, say, 1 mm. the order of the potential is 1000 volts.

According to our observations the specific charge depends considerably on the distance of its metallic surrounding (as already stated by Eguchi). The charge is high only so long as the electret is short-circuited. As soon as the metallic covers are removed the measured charge very soon becomes considerably reduced. Used without qualification the specific charge q , which characterizes the electret, usually means the specific charge of the *shorted* electret. The measurement of it has to take place very shortly after the upper plate has been removed, to prevent the decrease of q , which lasts some time.

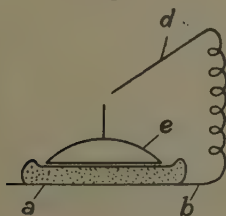
This fact is of great importance in considering applications of the electret. Only the field between it and a rather close metallic plate can be utilized. When the corresponding condenser plate is remote the field obtained is small.

Another point is important in this connexion: it might be thought that it is possible to charge some other condenser with the electret and utilize this secondary field. This, however, is impossible; if another condenser is charged with the electret, for instance as shown on fig. 3, the charge of this latter will last for only a limited time. The inevitable losses of even the best possible condenser will soon destroy this charge and a new charging procedure will be necessary.

The electret is not a battery. One cannot use it instead of a battery for charging a condenser or any other appliance, for instance the grid of a valve. The electret does not do by itself any work. When another condenser is charged by it, the necessary energy is supplied by the work done in removing the plate from the electret.

It is possible to demonstrate this by the following experiment (fig. 4). An electret *a* is placed on a metallic plate *b*. A metallic frame *e* with a plate on its bottom and a needle at the top is dropped on the electret. The opposite charge is induced at the bottom plate and an equivalent charge is collected in the top part. (If the frame is gently placed, instead of dropped, on the electret, the top charge would be immediately carried away.)

Fig. 4.



Sparking device for electrets.

If another needle *d* connected with the plate *b* is now approached to the needle on *e* until the points are something like 1 mm. apart, a tiny spark discharge takes place. This discharge can be repeated, theoretically without limits. (Practically a limit is set, by diminishing *q*, the electret not being always shorted.)

The energy of the spark is supplied in this experiment by the work done against the electric forces in lifting the frame after each experiment.

It is necessary to use for this experiment somewhat larger pieces, about 8 cm. in diameter. The arrangement is quite useful for quickly checking whether an electret is sufficiently charged. Good samples give sparks of about 1 mm.; poorly charged ones give a just detectable spark; and bad samples do not spark at all.

A last very important point to be mentioned in this general characterization is the question of humidity.

The electrets are very sensitive to humidity. Only specimens kept entirely dry, by means of calcium chloride or phosphorus pentoxide, keep their charges satisfactorily. Shorted samples kept in the open air are still good so long as the relative humidity does not exceed, say, 80 per cent. During the summer months, therefore, it is rather inadvisable to keep them open.

The effect of humidity consists in covering the pieces with a microscopically thin water layer, which, of course, acts as a conducting sheet and simply shields any field on the electret surface. When a moist sample is brought back in a dry chamber it gradually recovers and regains its effectiveness. On the other hand, it has been observed that samples after a more prolonged period in a humid atmosphere, especially if during that time they have not been short-circuited, may suffer a more serious damage. They do not recover even in a dry chamber. Probably water penetrates into the interior and destroys the electrification of the bulk. This penetration may take place either through minute pores or is simply a common absorption.

The high sensitivity of the electret to humidity is certainly a drawback from the practical standpoint. When used in any apparatus this always has to be kept close and internally dried by a suitable agent.

4. *Mechanism of the Hetero-effect.*

Having given a general description of these bodies, some experiments will now be outlined which allow certain conclusions to be drawn as to the nature of the heterocharge.

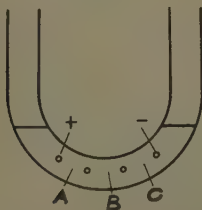
As already mentioned, this does not usually constitute the final charge, but is present initially and generally fades away. This behaviour leads to the suggestion that its mechanism is ionic. Joffe ⁽⁴⁾ has shown that in solid dielectrics (*e. g.*, glass) an accumulation of oppositely charged ions near the electrodes takes place while current is flowing. By means of ballistic measurements the author ⁽⁵⁾ has demonstrated this kind of space charge in oils, immediately after removing the voltage. It seems very probable that the same phenomenon will occur in fluid wax which is solidifying while voltage is still on. The ions are captured in their position and manifest themselves as a heterocharge.

Owing to the small conductivity of wax in the solidified state there will be a slow neutralization of these space charges, which accounts for the slow dissipation of the heterocharge.

This hypothesis can be verified in two different ways. One of the proofs is chemical, and will be discussed in Section 6. The other consists in a measurement of the potential distribution during solidification and clearly shows the correctness of our assumption.

A glass vessel with four connexions was used (fig. 5). It had the shape of a U-tube and contained four platinum wires, shown diagrammatically in the figure. The tube was filled with melted wax and then immersed in an oil bath, which slowly cooled down. The two external wires served as leads for the high tension, while the

Fig. 5.



Tube with probes for space-charge measurements.

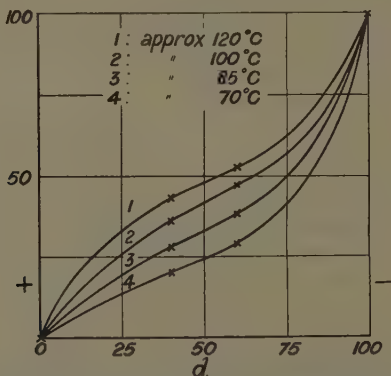
internal wires functioned as exploring electrodes. Owing to the form of the field the drop of potential could not be expected to be uniform. The vessel was therefore calibrated with a liquid possessing a high conductivity at room-temperature, exhibiting therefore no appreciable space-charge effect (a mixture of alcohol and benzene). This preliminary measurement revealed that the resistances in the spaces A and C were twice as large as in the space B.

The measurement of potential was carried out by means of a static voltmeter. The total voltage used was of the order of 500 volts D.C. All the three voltages A, B, and C have been measured.

Measurement has been taken at four different temperatures. The starting temperature was 120°C ., the mixture was cooled down until 70° . Solidifying takes place somewhere about 80° .

The result is shown on fig. 6, which shows the potential distribution for four temperatures between 120° and 70° . Owing to the calibration values of the vessel the potential drop A occupies 40 per cent. of the total abscissa starting from the positive electrode, B the following 20 per cent., and C the last 40 per cent. It can be seen that the distribution is very unhomogeneous, revealing large space charges. It is unsymmetrical with respect to the two electrodes, the drop being greater at the negative than at the positive electrode. Moreover, the unsymmetrical behaviour becomes more and more pronounced

Fig. 6.



Potential distribution in electrets during making.
(Both potential ϕ and distance d are arbitrary units.)

as the temperature decreases. In the solid state only the drop at the negative electrode is distinctly visible.

At the higher temperatures there is an accumulation of carriers of opposite sign at both electrodes. In the solid state there is a distinct positive space charge at the cathode, whereas the corresponding negative space charge is rather small and therefore extends far into the bulk. The reason for this behaviour is the different mobility of the kations and anions. They are rather similar at the higher temperature, but the mobility of the kations is considerably greater than of the anions at lower temperatures. Most of these materials being

high molecular organic acids they dissociate into hydrogen ions and large organic anions. Hence the difference in their mobility is quite understandable. The more mobile hydrogen ions are gathering near the cathode, thus forming the positive space charge, whereas the inert anions stay where they are, uniformly distributed over the whole volume.

This experiment proves clearly that there is a considerable space charge after the wax is solidified, the sign of which agrees with the observed heterocharge. It cannot last very long, as the mobility of ions is still finite at room-temperature, and neutralization will take place in a finite time.

If this explanation be right it is possible to estimate the life of the heterocharge. The specific resistance of a good insulator is of the order of 10^{18} ohms cm., while the specific capacity is about 10^{-12} farad. The time constant is therefore of the order of 10^6 sec., *i. e.*, approximately 10 days. With this value the period at the end of which the charge has only 2 per cent. of the original amount is some 40 days. It will be shown in Section 6 that the observations agree quite well with this order.

In this connexion the question can be raised whether an electret as a whole would show any charge in a Faraday chamber. This is theoretically possible; if the arrangement is not quite symmetrical one of the two space charges may prevail. In the apparatus shown on fig. 1. for instance, the field, and correspondingly the space charge at the upper electrode, will be higher. In a recent investigation P. Jaeger ⁽⁶⁾ observed this effect.

5. Mechanism of the Homocharge.

The steady charge, which is usually a homocharge, is more difficult to understand than the temporary heterocharge. Whereas the latter is due to molecules which undergo an electrolytic dissociation and form ions, the former seems to be due to non-dissociable components, which, on the other hand, have a finite dipole moment. The materials showing the effect (see next paragraph) are mainly hydrocarbons, containing esters and alcohols. It is probable that these latter form crystalline nuclei in the more or less glassy medium.

Whereas normally the orientation of these crystallites is a disordered one, they obtain a definite orientation

if crystallization takes place in an electric field. This is due to the fact that the elementary molecular aggregates building up the cell unit of the crystal often exhibit a finite dipole moment. These become oriented, and, consequently, the crystals growing along these nuclei as well.

There are several papers which show clearly such possibility. R. D. Bennett ⁽⁷⁾ could show it for paraffin wax by means of X-ray investigation, as well as M. Ewing ⁽⁸⁾ for materials capable of building electrets.

The crystallites being oriented and the mixture cooled down further, the surrounding wax solidifies and keeps the crystals in their oriented position. They are captured in this state, and as carnauba wax especially is extremely hard at room-temperature, they cannot change their orientation or, if they can, do so at a very slow rate.

So far it seems as if the question were already answered. The primary reason for the orientation was the finite dipole moment of the molecules, and they must exhibit a certain free charge, even after removal of the polarizing field. But this charge ought to be evidently a kind of heterocharge, and is therefore inconsistent with the observed sign of the steady charge. This fact indicates that the steady charge is not directly given by the oriented dipole moments.

E. P. Adams ⁽⁹⁾ considers in a paper the same point, and gives the following explanation. The heterocharge of the crystals becomes neutralized through accumulation of ions on the surface. Owing to a slight but continuous decay of the orientation of dipoles and to a certain retardation of the corresponding decay of the surface charge, the sign of the latter always prevails. Although this explanation is rather attractive, we should like to point out an alternative theory and this for the following reason. The time constant of the decay of orientation is certainly large, at all events larger than the time constant of ionic motion on the surface. The latter ought to follow the former almost instantaneously, and, assuming for the polarization of the dielectric a reasonable value (certainly much less than 10^5 abs. as assumed by Adams), the observed free charge ought to be much smaller than indicated by experiment.

Moreover, it appears that molecules are usually so arranged in a crystal that their resultant moment becomes small.

It seems, therefore, probable that, although the orientation of crystallites is the primary reason, there must be another effect leading to the homocharge. This effect is very probably in connexion with a piezoelectric property of the crystallites. That there is such a connexion has already been suggested by Adams, who even succeeded in detecting a piezoelectricity in electrets with a highly sensitive Dolezalek electrometer.

We also tried to show its existence by means of the equipment shown on fig. 3. Pressure was applied by means of a sphere in order to increase the stress per unit area. However, the relatively low sensitivity of our electrometer (necessary to measure the large charges of the electrets) was apparently not sufficient for this purpose, though several kgm. weight were applied.

A piezoelectric effect in other dielectric materials has been shown experimentally by A. Turpain and M. Durepaire⁽¹⁰⁾, especially for caoutchouc and ebonite. A paper of A. Meissner and R. Bechmann⁽¹¹⁾ has also to be mentioned in this connexion. They suspended powdered quartz in waxes and detected a high piezoelectric constant in the mixture solidified and oriented under an electric stress. This proves quite clearly that it is possible to produce artificially an axis of optical symmetry in a piezoelectric mixture of originally random distribution.

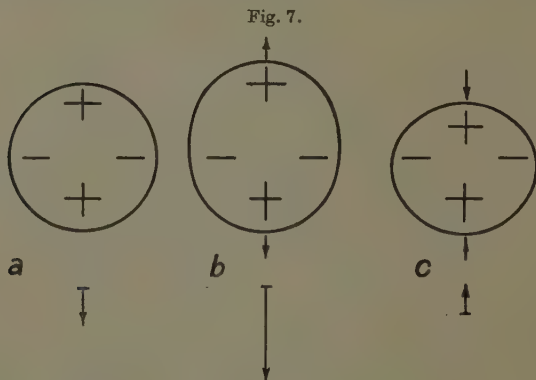
Assuming this to hold for our electrets as well, it is only a step further to account for a continuous piezoelectric moment. This possibility is suggested by the considerable brittleness, that is, internal stress of the electrets. If no care is taken to allow for a contraction during cooling by covering the electrodes with tin-foil, they inevitably split into pieces. Even so, they very often break. This is evidently a sign for a strong internal stress in the material. The extent of this tension can be seen on broken electrets, namely, by the distinct crevices visible after the pieces have been exactly replaced together.

The mechanism of the development of an internal tension is the following. The coefficient of thermal expansion is very large. Contraction of the material is not impeded parallel to the field owing to the yielding tin-foil. But it is hindered in its radial contraction perpendicular to the field, as the surrounding mixture will cool down first

and does not allow for a sufficient contraction of the central portions. Hence a strong radial tension is originated, which will not be released in a hard material like carnauba wax. It will behave like a radially stretched circular disk.

We tried to show the importance of this fact by changing the cooling conditions during the making of the electret. Unfortunately, all variations only increased the stresses, causing the samples to break during the process.

A radial stress being accompanied by a deformation, namely, a contraction parallel to the axis, there will be a free charge on the surfaces perpendicular to the



Piezoelectric explanation of homocharge.

axis if the material is piezoelectric. All we have to assume is, that the piezoelectric charge is opposed to that of the original dipole in order to account for the homocharge. To show that more rigorously, very detailed investigations on several piezoelectric crystals, such as that of Sir W. H. Bragg and R. E. Gibbs ⁽¹²⁾ on quartz, would be necessary.

At all events, the general rule, which is in keeping with that assumption, is the following. The polarity of the piezoelectric moment of a crystal is, for extension, the same as that of the original dipole moment of the elementary molecule, and the opposite for compression.

The plausibility of this rule is shown by fig. 7 for a quadrupole molecule as basic element. Suppose it possesses in the normal state (*a*) a finite dipole moment (shown by the arrow) owing to a greater freedom of motion of one of its positively charged atoms. Extension of the lattice must therefore result in an increase of the original moment (*b*), compression in its decrease and even reversal (*c*). That is in accord with the above rule and the observed sign of the charge. It is also in keeping with the theory that there is a possibility of a steady heterocharge, namely, if the piezoelectric moment is not strong enough to reverse the original polarity (see next paragraph).

Summarizing our explanation, the mechanism of the homocharge is as follows. The molecules of the crystalline components possessing a finite dipole moment orient in the field, thus causing a symmetry of crystallization (axis parallel to field). The crystallites being piezoelectric, the whole electret assumes this property. Owing to contraction during cooling a strong radial tension will be established in the material, being equivalent to a compression of the lattice parallel to the field. This reverses the original polarity, and as the tension is not released the moment is a permanent one.

The role of external ions remains to be explained. One generally assumes that they very soon neutralize any piezoelectric charge. Now this is the case with the electrets as well, if they are kept open. Only by being kept in a dry atmosphere, thus minimizing the surface conductivity, will they maintain their efficiency.

Moreover, they have to be kept short-circuited, thus minimizing the stray field parallel to the free surface and the possibility of attracting ions of opposite sign. They are thus somewhat similar to permanent magnets, which are also best kept shorted.

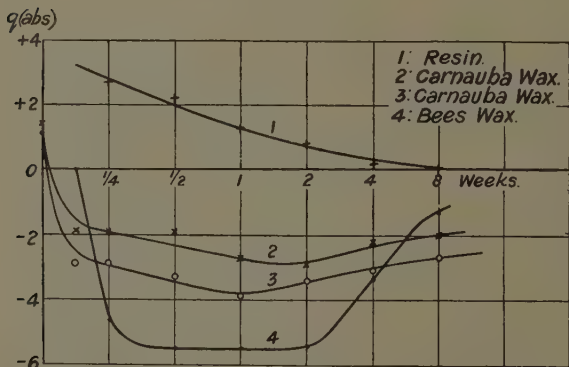
It is quite possible that if a quartz crystal were to be kept under similar conditions, not releasing the external pressure, it would always exhibit a similarly constant moment. The difference lies only in the circumstance that the pressure in an electret is an internal one.

The explanation given in this section is only a kind of working hypothesis, which needs further experimental confirmation.

6. *Effect of Chemical Components on the Electret-effect.*

The following is a summary of some measurements carried out with electrets of different chemical composition in order to find out the rôle of the single constituents. The results are presented in three graphs, figs. 8-10, showing the specific charge q in absolute units as a function of time. The latter is marked in weeks on a logarithmic scale. The method of measuring is that of Section 2 (b). The electrets in question were kept always shorted and measured quickly after lifting the upper plate. They were kept in a normal room

Fig. 8.



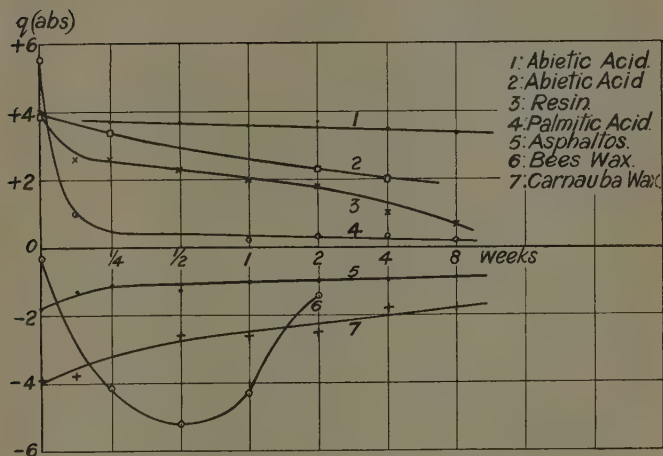
Charge of electrets against time. (Single materials.)

atmosphere; the values would be different if they had been kept in a dry chamber, but since the purpose was a *comparative* measurement, this point was not very important.

The first graph, fig. 8, shows the three most important materials alone: resin, carnauba wax, and beeswax. There are two sets for carnauba wax.

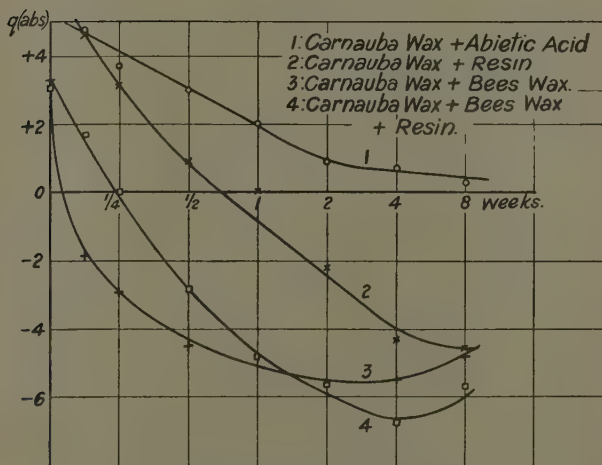
The second graph, fig. 9, shows several materials all dissolved to some 15 per cent. in paraffin wax. As a previous measurement showed, the latter has no appreciable charge at all, and is therefore quite suitable as an indifferent medium. The solutes were: carnauba wax, beeswax, resin, abietic acid (two sets), palmitic

Fig. 9.



Charge against time. (Solutions in paraffin wax.)

Fig. 10.



Charge against time. (Mixtures.)

acid, asphaltos, cetyl palmitate, cetyl alcohol, Seekay wax ⁽¹³⁾, and stearanilide. The four latter specimens are not represented in the graph, as they exhibited no appreciable charge.

The third graph, fig. 10, contains four mixtures, namely : carnauba wax + resin, carnauba wax + abietic acid, carnauba wax + beeswax, carnauba wax + beeswax + resin. The proportions were respectively : 1 : 1, 1 : 1, 2 : 1, 1 : 1 : 1.

The following conclusions can be drawn :—

(1) There are two types of constituents. One shows only a heterocharge. All pronouncedly acidic materials belong to this group. It has to be borne in mind that resin is mainly some 90 per cent. abietic acid. The other type shows mainly homocharge, sometimes with a very short life heterocharge in the beginning. All the esters and hydrocarbons belong to this type. It is worth mentioning that carnauba wax is a vegetable wax containing mainly esters of myricyl alcohol, carnaubic acid, and cerotic acid, just as beeswax contains myricyl alcohol, ceryl alcohol, melissic acid, and cerotic acid. They contain a smaller percentage of free acid and alcohol as well. Asphaltos is a high molecular hydrocarbon.

This result is a valuable proof for the explanation of both effects given above. In acids there is a relatively large electrolytic dissociation in ions, and occurrence of space charges of the kind described is therefore very probable. In these materials a heterocharge is originated.

In the case of esters or hydrocarbons no dissociation takes place. The ion content is accordingly small, coming only from acidic impurities. On the other hand, they possess a finite dipole moment, and the orientation of the molecules in the liquid state leads to an oriented crystallization. A homocharge will result according to the mechanism described in the foregoing paragraph.

(2) There is evidence for an addition law for mixtures. Curve 2 on fig. 10 shows distinctly, if not quantitatively, the addition from curves 1 and 2 on fig. 8. At first the heterocharge of the resin prevails, and later on becomes replaced by the homocharge of the carnauba wax. In curve 3 in fig. 10 the homocharge is greater from the start, owing to the higher values of the beeswax in curve 4 of fig. 8. Again, an addition of resin (curve 4, fig. 10)

shifts the value towards the positive region in the first week. Curve 1 of fig. 10 shows only positive charges. If one compares abietic acid with resin (curves 1, 2, and 3 in fig. 9), the shifting is immediately understandable.

The very pronounced change in sign of a carnauba wax-resin electret, already observed by Eguchi, has therefore no electrical meaning whatever. It is simply an additive phenomenon, owing to the different behaviour of the two components.

This fact suggests that a kind of addition may occur not only in mixtures but also in other single materials which are mixtures in reality. Thus the early parts of curves 2 to 4 in fig. 8 indicate the presence of a space-charge effect which rapidly fades away.

(3) Concerning the question of the variation of charge with time it may be emphasized that the curves relate to humid air, and therefore do not give the optimum conditions. This is, perhaps, the reason why carnauba wax alone does not keep constant. (For constancy, compare Section 7.)

A slow decrease with time is generally observed in both types of charges. It does not appear possible to deduce a simple law governing the decay. The time constant for resin and palmitic acid seems to be of the order of 1 or 2 weeks, as estimated in Section 4. Abietic acid has a much larger time constant, the reason for which is probably that it is not an ionic but a dipolic charge, the sign of which is not reversed by the piezoelectric effect. As for the homocharge, only the hardest materials seem to be good enough to produce long-living electrets. Paraffin wax and beeswax are far too soft for this purpose.

It will probably be useful to carry out measurements of this type on a possibly large scale of materials and with a possibly high accuracy. It is not impossible that the measurement of the homocharge of electrets will prove a useful aid in exploring the structure of organic materials.

In order to carry out exact determinations of this kind several conditions have to be fulfilled :—

(a) It is necessary to possess a matrix for all kinds of solutes, which is itself absolutely indifferent and has the highest possible melting-point. Paraffin is too soft

for this purpose. Perhaps one of the new synthetic materials, such as Trolitul for instance, will do.

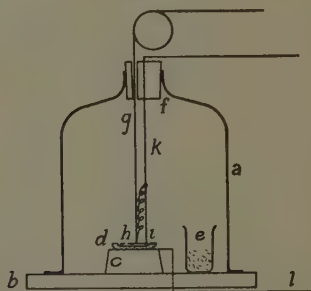
(b) The measurements must be taken under well-defined conditions; besides the use of a dry chamber, the distance between electret and plate has to be kept possibly small, as the charge depends on it (see apparatus described in next paragraph).

(c) For a given wax, as indifferent medium, a kind of calibration could be made by suspending in it a material of known piezoelectric constant.

7. Applications of the Electret.

This question will be touched only briefly, since it is intended to treat it in detail elsewhere.

Fig. 11.



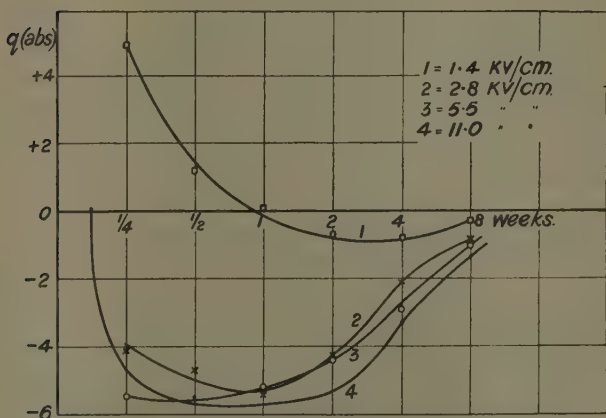
Dry chamber for measuring an electret.

The most important point in this connexion is the duration of the charges. Eguchi mentions three years. Two specimens (carnauba wax-resin mixture) have been kept in our experiments under the optimum conditions, that is, in dry chambers, dried with calcium chloride, and short-circuited. One of them was taken out from time to time and tested with the sparking arrangement shown on fig. 4. The length of the spark did not diminish during observations lasting a year. In the meantime the specimen was kept once in moist air, whereupon the sparks considerably decreased. But it recovered again when placed in the dry chamber.

Another sample was measured from time to time with the apparatus on fig. 3, but during its stay in

a dry chamber. This seems to be the ideal arrangement for exact measurements; the dry chamber is shown on fig. 11. It consists of a bell-jar *a*, resting on a wooden disk *b*, and containing a paraffin block *c* on which rests the electret *d*. There is also a vessel with calcium chloride *e*. The thread *g*, which lifts the measuring plate *h*, passes through the stopcock *f*. There is also a guard-ring *i*; from both *h* and *i* a wire connexion *k* leads to the earthed part of the electrometer. The wire *l* leads from the lower plate to the isolated part of the electrometer.

Fig. 12.



Charge against time for 15 per cent. beeswax in paraffin.
(Different polarizing voltages.)

In this arrangement the specimen was measured during a year without showing any decrease in its charge, the latter being some 6.5. This corresponds to a field strength of 24 kv./cm., nearly the breakdown strength of air, the highest possible field on a free surface.

Another question of some importance is, what field strength is necessary in order to make electrets of high charge. For this purpose a series was taken with 15 per cent. beeswax in paraffin wax, in which the polarizing voltage was varied. The result is shown on fig. 12. The field varied from 11 to 1.4 kv./cm. There is distinct

evidence that the curve relating charge with polarizing field shows a kind of saturation phenomenon, the nature of which, however, is not clear. A field of 5 to 10 kv./cm. seems to yield sufficient charges, though a further small increase with increasing voltage is not impossible.

Two of the possible applications should be mentioned here shortly. One would be in electrometers. Instruments of the Dolezalek type, for instance the Lindemann electrometer ⁽¹⁴⁾, need an auxiliary field. The sensitivity increases with increasing strength of this field. Now the latter could be supplied by means of electrets; the same is possible for any kind of string-electrometer. The string could be stretched between a pair of electrets, the free surfaces of which being positive and negative, producing in this way the necessary field.

Another type—this is a suggestion of Mr. E. B. Moullin—could be built as an analogy to a mirror-galvanometer. A freely suspended electret represents an electric dipole; if it is placed between two plates which are charged to the potential to be measured the electret undergoes a certain displacement which can be measured by a mirror and scale. A roughly built electrometer of this type displayed a sensitivity of 0.5 volt per division.

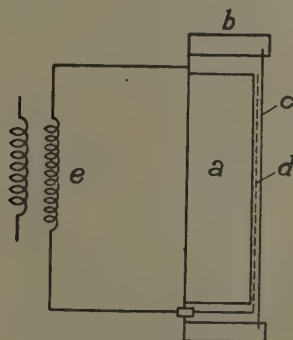
Instruments of relatively lower sensitivity, but of a more robust type, can also be made on the same principle; a model built by us had a sensitivity of some 10 volts per division. The general advantage of these instruments is the linear scale and very small capacity.

A second application is their use in microphones or loud-speakers, on the principle of condenser microphones. When used in the low-frequency circuit devised by Wenté these require a charging battery. This can be avoided if a free electret surface is used opposite the vibrating membrane. In this case it is not so much the change in capacity which is utilized, but the alternating change in the influenced charge, which causes an alternating current in the connected circuit.

The principle will be better understood by means of fig. 13. *a* is an electret enclosed in the casing *b*; its free surface faces the diaphragm *c* a small distance apart, joined metallically with the casing. The same surface is coated with a metallic mesh *d*, insulated from the casing. Diaphragm and grid lead to an outer circuit, for instance a transformer *e*. Both diaphragm and mesh

possess a certain capacity against the free electret surface. The ratio of their influenced charge depends on the ratio of their partial capacities. When the diaphragm moves, as a result of a sound wave for instance, the capacity ratio changes and in the same manner changes the charge ratio. There will be an alternating current in the transformer, which for small amplitudes has the same wave form as the acoustical wave. The apparatus acts therefore as a microphone.

Fig. 13.



Electret microphone.

I am much indebted to Sir William Bragg, O.M., K.B.E., F.R.S., for his kind and helpful criticism, to Prof. R. V. Southwell, F.R.S., for facilities placed at my disposal in the Engineering Laboratory at Oxford, to Mr. B. L. Goodlet in Manchester for many stimulating discussions, and to Messrs. Metropolitan-Vickers Elec. Co., Ltd., Manchester, for a grant enabling this investigation to be carried out.

8. Summary.

1. The work of Eguchi concerning constantly electrified bodies, so-called electrets, has been extended. The method of preparation and the measuring equipment are described. The main results of Eguchi are verified.

2. Electrets are the electrical analogues of permanent magnets, and the field on their free surfaces can accordingly be utilized provided that they are nearly short-circuited and kept dry.

3. There are two possible kinds of charges. One has the opposite sign to the adjacent polarizing electrode: the heterocharge. It is usually of short duration; it is probably caused by ionic space-charges. Probe measurements on electrets during solidification verified this assumption.

4. The other type of charge has the same sign as the adjacent polarizing electrode: the so-called homocharge. It is caused by orientation of dipole molecules, leading to an oriented crystallization and accompanied under circumstances by a secondary piezoelectric effect. This effect is the steady one. Its exact measure will probably be a valuable method for exploring the structure of organic molecules.

5. The influence of different chemical constituents on the effect has been investigated. In conformity with the theories put forward acidic materials, yielding ions, produce a heterocharge, while non-dissociating dipoles, chiefly esters, lead to the steady homocharge. For mixtures an addition law has been found to be valid.

6. Concerning technical applications it has been shown that electrets really keep their charge if stored under proper conditions. The making field strength during solidification has to be some 5–10 kV./cm. Two possible applications are: for electrometers with a linear scale, and for a kind of electrostatic microphone.

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LXXIV. *The Measurement of Small Amplitudes of Vibration.* By G. F. PARTRIDGE, B.Sc., F.Inst.P.*

THE measurement of the amplitude of vibrations is of fundamental interest in connexion with the study of sound transmitters and receivers. Of the various methods of measuring small deflexions few are applicable to the measurement of vibrations, so that several special methods have been evolved.

In connexion with an investigation into the modes of vibration of telephone diaphragms Kennelly ⁽¹⁾ developed an amplitude explorer, using a small mirror and optical magnification. With this he was able to measure amplitudes of the order of 10^{-5} cm. with precision. Thomas and Warren ⁽²⁾ have used an optical method, employing fringes of monochromatic light, which is capable of determining amplitudes of the order of $0.5.10^{-6}$ cm. Another method has also been described by Thomas ⁽³⁾ in which the vibrations are caused to produce eddy current effects in a tuned valve circuit.

In 1919 Sir William Bragg ⁽⁴⁾ and ⁽⁵⁾ described a simple mechanical method of measuring amplitudes, making use of a vibrating reed. This method has recently been used by Strutt ⁽⁶⁾ in an investigation into the behaviour of loud-speaker diaphragms at acoustic frequencies. These measurements were made with amplitudes of the order of 10^{-3} cm.

The measurements described below were made shortly after Bragg suggested the method, and show that by using a rigid pendulum instead of a reed it is possible to measure amplitudes of the order of 10^{-6} cm.

In order to test the accuracy of the method it will be seen that it is desirable to have as a source of vibration a transmitter whose amplitude can be calculated. For this reason a quartz strip vibrator was used at acoustic frequencies. This has the advantage of a supersonic natural frequency, and, provided it is driven at constant voltage, a constant amplitude at acoustic frequencies.

(1) *Method of Measurement of Amplitude.*

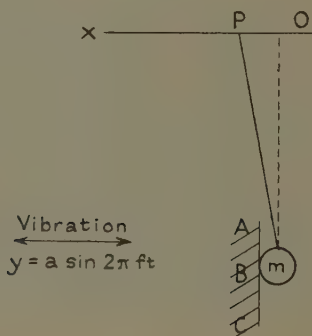
The principle underlying the method is as follows : Imagine A, B, C (fig. 1) to be a section of a surface vibrating

* Communicated by the Author.

in a horizontal direction, and B the point at which the amplitude is to be measured. A mass m , forming part of another vibrating system, is caused to exert a pressure against the surface at this point. This pressure is obtained by any suitable means, as, for instance, by means of a reed, as originally suggested by Bragg, or, as in the figure, where m is the bob of a pendulum suspended from a support which can be moved along a line O P X parallel to the direction of vibration.

O is the position of the support when m is touching the surface of the vibrator before the latter is set in vibration.

Fig. 1.



Let the surface be given an amplitude y and the support moved inwards towards the surface a distance d .

The equation of motion of the mass m is given by

$$m\ddot{x} + r\dot{x} + c(d+x) = P, \quad . \quad . \quad . \quad (1)$$

where m , r , and c are the mass, damping factor, and control factor of the pendulum, P the pressure between the surface and the pendulum, and m and x the mass and amplitude of vibration of m .

In the measurements which follow it can be assumed that the stiffness of the vibrator is much greater than c , so that there is no bodily displacement of the surface due to the pressure P . Under these conditions $x = y$.

$$\text{Putting } x = y = a \sin \omega t = a \sin 2\pi ft,$$

where f is the frequency of the applied vibration, and taking the damping as negligible we have

$$-m\omega^2 a \sin \omega t + c(d + a \sin \omega t) = P.$$

As long as P is positive, *i. e.*, inwards towards the surface, the mass m remains in contact with the surface. If P at any time becomes negative the mass leaves the surface and following its own free motion subsequently returns to the surface. This process is repeated indefinitely, producing a "chatter" between the mass m and the surface. If now d is gradually increased a point is reached when chattering just ceases.

This occurs when $P=0$ and $\sin \omega t=1$. The relation between a and d is then given by

$$-m\omega^2 a + c(d + a) = 0$$

or
$$a = \frac{cd}{m\omega^2 - c} = \frac{\omega_0^2 d}{\omega^2 - \omega_0^2},$$

since
$$c = m\omega_0^2 = m \cdot 4\pi^2 f_0^2,$$

where f_0 is the frequency of the pendulum.

This suggests the method of measuring the amplitude a . Starting with m free of the surface and the latter not vibrating the support is moved until m just touches the surface, and its position noted. The surface is then set in vibration and the support again moved inwards until chattering ceases, and the position noted. The distance between these two positions gives d . The value of a then follows, knowing ω and ω_0 .

If ω_0 is small compared with ω the value of a is approximately given by

$$a = \frac{\omega_0^2}{\omega^2} \cdot d = \frac{f_0^2}{f^2} \cdot d. \quad . \quad . \quad . \quad . \quad (2)$$

For a given amplitude a the value of d depends upon the factor f^2/f_0^2 , which may be termed the "amplification factor." In order to measure small amplitudes this factor must be large. It follows that f_0 must be small, its value being determined with a view to bringing d within reasonable measurement.

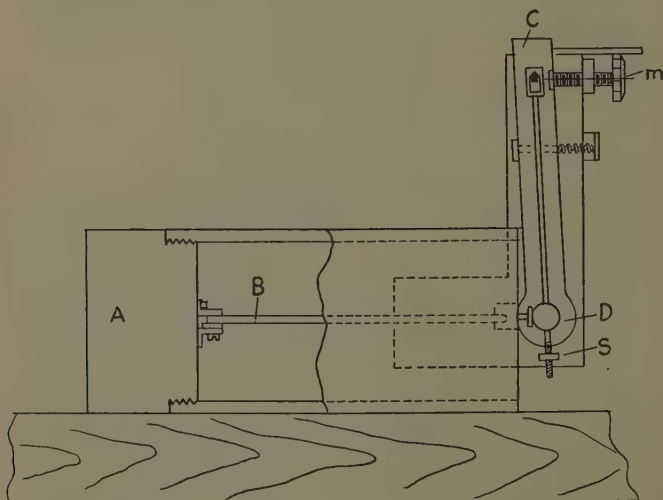
Thus in order to measure amplitudes of the order of 10^{-6} cm. at a frequency of 1000 p.p.s., and give say a displacement d of 0.10 cm. the required magnification is

$$\frac{d}{a} = 10^5, \text{ i. e., } f_0 = 3.3 \text{ pps.}$$

(2) Experimental Arrangement.

It is essential to have a rigid support for the pendulum. It has been possible to obtain this by fixing the vibrating strip to a massive block, the pendulum being supported from a hinged member also attached to the block. The arrangement is shown in fig. 2. A is the block and base, B the vibrating strip, CD the pendulum support hinged at D, a point approximately on a normal to the diagram passing through the centre of the pendulum bob. This

Fig. 2.



arrangement provides a displacement of the support without disturbing the point of contact of the bob.

The displacement of the support is measured by means of a micrometer screw *m*, each division corresponding to a movement of 0.01 mm.

Various optical and electrical methods of determining the contact have been examined. An electrical method has been found most satisfactory, employing the circuit given in fig. 3. A pair of 4000 ohm telephones are connected in series with a 2 volt cell and a 5000 ohm resistance, and the circuit through the vibrating surface and the

pendulum form a shunt to the telephones. The pendulum contact and the vibrating surface are silver-plated. With this arrangement the point at which "chattering" ceases can be determined very definitely by listening in the telephones.

(3) Experimental Results.

At the outset attempts were made to use a vibrating reed as the measuring device. The frequency of a loaded phosphor-bronze reed at low frequencies is given very nearly by the formula

$$f^2 = 7.8 \times 10^9 \frac{t^3}{l^3} \cdot \frac{b}{m},$$

Fig. 3.

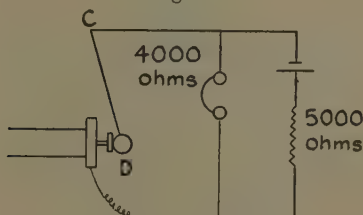


TABLE I.

Frequency of Reed 1.66 p.p.s.
 $a = 2.75 d/f^2$.

Frequency of vibration= f .	600.	700.	800.	900.	1200.
Displacement of support in mm.= d .	0.24	0.39	0.85 1.10	1.62 1.68	3.10
Calculated amplitude= a in cm. $\times 10^{-6}$	0.18	0.22	0.36 0.47	0.48 0.49	0.59

where l , t , and b are the length, thickness, and breadth of the reed and m is the mass of the load. It will be seen that for a reed of frequency about 2 p.p.s. the ratio t/l must be very small unless m can be large. It can be shown that the mass m must be relatively small compared with the effective mass of the vibrator. A suitable value in the present case is found to be about 1 gm., and for this value $t/l = 10^{-3}$.

Such a reed was made, and as the measurements are of interest a few of the results are given here.

As mentioned previously the vibrating surface was driven at constant amplitude. This amplitude, as determined from the constant of the vibrator, knowing the dimensions of the vibrator and the applied voltage, has the value of 1.01×10^{-6} cm.

It will be seen that all the values of a derived from the observed values of d are lower than the above value. The results suggest that the factor $2.75/f^2$ which has been used in calculating the values of a is too low—in other words, the reed is exerting a pressure corresponding to a higher frequency than its fundamental. It is very probable that this is the explanation, for, due to the

TABLE II.
Frequency of Pendulum 1.73 p.p.s.
 $a = 2.99 d/f^2$.

f .	900.	1000.	1100.	1200.	1300.	1400.
d in mm.	0.27	0.38 0.35 } 0.43	1.05	0.47 0.46 } 2.1		
a in cm. $\times 10^{-6}$	1.00	1.13 1.05 } 1.06	2.18	0.83 0.82 } 3.2		

weakness of the control and the relatively heavy load. the reed could readily be forced into harmonic vibration,

As an alternative to the reed we may use a rigid lever hinged about O and controlled either by means of a spring or gravitationally. The latter arrangement is in effect a pendulum, and where practical conditions permit is preferable to the former, since this with weak control suffers to some extent from the same defect as the reed.

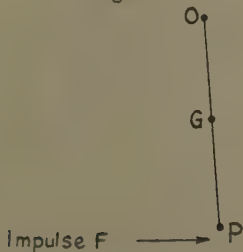
The pendulum which was first used consisted of a hollow ball of about 1 cm. diameter attached to a brass rod of about 1.5 mm. diameter, supported at its upper end on a knife-edge bearing. In order to provide an electrical connexion for the detecting circuit the bearing was bridged by a fine wire spiral.

Some of the results obtained with this pendulum are given in Table II., from which it will be seen that the amplitudes calculated from the observations agree more

nearly with the expected amplitude than in the case of the reed measurements, except at the higher frequencies.

When the ball of the pendulum is chattering on the vibrating surface there are impulsive blows at the point of contact; the intensity of which increases with the square of the frequency. Any impulsive reaction therefore upon the knife-edge support would be more marked at the higher frequencies. This was considered to be the reason for the uncertainty in the vibrations at the higher frequencies. To check this the wire connecting the seating and the pendulum was replaced by the detecting circuit, when it was found that there was definite chattering between the knife-edge and the seating, which became very violent at the upper end of the frequency range.

Fig. 4.



With a body of such simple form the behaviour under the influence of impulsive blows can be worked out theoretically. It can be assumed that the problem is a two-dimensional one and that the centre of mass and the point of application of the blow are in a principal plane of the pendulum.

In fig. 4 let OGP be a line in this plane, where a normal through O is the line of contact of the knife-edge and support, G the centre of mass, and P the point of contact. Assuming that the pendulum can be regarded as a rigid body, it can be shown that the initial velocity at the point O, due to an impulse of strength F at P, is given by

$$v = \frac{F}{M} \left[1 - \frac{a(l-a)}{k^2} \right],$$

where k = radius of gyration about G,
 M = mass of pendulum,
 l = OP and a = OG.

flexible loud-speaker diaphragms, in which case it becomes of importance.

It will appear from the results of the Appendix that the method is not suitable for measurements at resonance.

The author wishes to express his indebtedness to the Admiralty for permission to publish this paper.

APPENDIX.

In the experiments which have been described the quartz vibrator was clamped at the one end and free at the other end.

Under these conditions the equation of motion is

$$M\ddot{y} + N\dot{y} + Cy = kV, \quad . \quad . \quad . \quad . \quad (1)$$

where

V = driving voltage ;

k = constant ;

M = mass of vibrator = $\rho b l t$;

N = damping factor ;

C = control factor ;

$$= 4\pi^2 \cdot f_0^2 \cdot M ;$$

where

f_0 = natural frequency of vibrator

$$= \frac{1}{4l} \sqrt{\frac{G}{\rho}} ;$$

l, t, b = length, thickness, and width of vibrator

= 7.0, 0.25, and 2.5 cm. respectively ;

ρ = density = 2.66 gm./cm.³ ;

G = Young's Modulus = 9.2×10^{11} dynes/cm.²

Inserting these values, we find that

M = 11.6 gm. ;

C = 2.02×10^{11} dynes/cm. ;

f_0 = 2.1×10^4 p.p.s.

Assuming that on applying pressure from the pendulum the free end of the vibrator is displaced inwards by a distance s cm., and that the amplitude of vibration is then x , the equation of motion becomes

$$M\ddot{x} + N\dot{x} + C(x - s) = kV - P, \quad . \quad . \quad . \quad (2)$$

where P is the pressure between the end-face of the vibrator and the pendulum.

From (1) and (2) we get by subtraction

$$M(\ddot{y}-\ddot{x})+N(\dot{y}-\dot{x})+C(y-x+s)=P. \quad (3)$$

The equation of motion of the pendulum gives us the following :

$$m\ddot{x}+c(x+d-s)=P, \quad (4)$$

where

m = mass of pendulum,

c = control constant of pendulum,

and d is the displacement of the support of the pendulum from the initial position.

Resonant Frequency of Quartz Vibrator.

Case (i.). *At Frequencies removed from f_0 .*

In this case the first two terms of (3) are negligibly small. Let $y=Y \sin \omega t$ and $x=X \sin \omega t$ in (3) and (4); then

$$\left. \begin{aligned} C(Y-X) \sin \omega t + Cs &= P, \\ (-m\omega^2 + c)X \sin \omega t + c(d-s) &= P. \end{aligned} \right\}$$

The condition when chattering between the pendulum and the quartz just ceases is satisfied when $P=0$ and $\sin \omega t=1$, i. e.,

$$\left. \begin{aligned} C(Y-X) + Cs &= 0, \\ (-m\omega^2 + c)X + c(d-s) &= 0. \end{aligned} \right\}$$

From these equations it can be shown that

$$s = \frac{cd}{C+c} \quad (5)$$

and

$$\begin{aligned} Y &= X - s \\ &= \frac{cd}{m\omega^2 - c} \left[1 - \frac{m\omega^2}{C+c} \right]. \end{aligned} \quad (6)$$

$Y = \frac{cd}{m\omega^2 - c}$ is the relation previously obtained by assuming that the quartz is unaffected by the pressure of the pendulum.

In the present case $m=1$ gm., $\omega=6000$, $c=86.2$ dynes/cm., and $C=2.02 \times 10^{11}$ dynes/cm., so that the correction term is of the order of .02 per cent.

Case (ii.). *At Frequencies near Resonance.*

It will be assumed that only the second term of equation (3) is negligible. We then have

$$\text{and} \quad \left. \begin{aligned} M(\ddot{y}-\ddot{x})+C(y-x+s) &= P \\ m\ddot{x}+c(x+d-s) &= P. \end{aligned} \right\}$$

Following the same procedure as in the previous case it can be shown that

$$s = \frac{cd}{C+c}$$

$$\text{and} \quad Y = \frac{cd}{m\omega^2 - c} \left[1 - \frac{m\omega^2}{C+c} \cdot \frac{1}{1 - \frac{\omega^2}{\omega_f^2}} \right],$$

where $\omega_f = 2\pi f_0$.

Here again the correction term is negligibly small up to frequencies very near resonance.

In both cases if the value of s is inserted in equation (2) when $P=0$, we get

$$(M+m)\ddot{x} + N\dot{x} + (C+c)x = kV.$$

Here c is negligible compared with C , but m is not negligible compared with M . The load m therefore has the effect of depressing the natural frequency of the vibrator.

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LXXV. *Examination of Electro-deposited Nickel Coatings by X-ray Diffraction.* By W. A. WOOD, M.Sc., *Physics Department, National Physical Laboratory, Teddington, Middlesex* *.

Introduction.

ELECTROPLATED nickel may exhibit hardness values from 180 to 400 Brinell according to the conditions of deposition ; similarly the brightness of the metal, taken direct from the plating bath, may range from a brilliant lustre to a dull grey appearance. The present paper summarizes the results of an investigation by means of X-ray diffraction upon a series of deposits which showed wide variations in hardness and initial brightness ; it points out differences in the X-ray diffraction spectra which appear to be associated with these modifications in properties, and which suggest that the X-ray method, utilized regularly for examining metallic coatings, would yield useful information of variables in structure not easily observed by other means.

Specimens.

The specimens of nickel plate were prepared by deposition on copper wire and copper plate. The wire, 20 S.W.G., was convenient for photographing the whole range of the spectrum at one time, and the sheet and bars for supplying plane surfaces for hardness measurements. The modifications in hardness of the deposits were obtained by varying the current density specimen to specimen on the lines shown by Macnaughtan ⁽¹⁾ ; differences in the lustre of the coatings resulted from the same procedure. Two types of bath were employed, made up according to the following formulæ :—(1) nickel sulphate 250 gm., sodium chloride 15 gm., and boric acid 25 gm. per litre of water ; and (2) nickel sulphate 50 gm., nickel ammonium sulphate 75 gm., and boric acid 25 gm. per litre. These were worked under conditions which allowed 500 c.c. of electrolyte to each square centimetre plated in order to maintain a reasonably constant composition throughout deposition. A preliminary cleaning treatment was given to the copper. It was first washed

* Communicated by Dr. G. W. C. Kaye, O.B.E., M.A.

in alcohol and benzene ; then made cathode for a short time in a bath consisting of 60 gm. sodium carbonate, 7.5 gm. sodium hydroxide, and 7.5 gm. sodium cyanide per litre of water ; and finally etched in nitric acid. A rod of electrolytic nickel was used as anode. The parts of the specimen which were not to take a deposit were coated with a protecting varnish made by dissolving celluloid in a mixture of amyl acetate and acetone. Sets of specimens were secured at current densities of 2, 4, 5, 8, 15, 20, 25, 30, 40, and 50 milliamps per sq. cm. from each type of bath at 14°-16° C. The hardness numbers, determined by a diamond pyramid test, varied from 176 to 460 ; the brightness from a brilliant to a grey matte type of deposit. It was found possible to correlate these variations with differences in the nature of the X-ray reflexion spectra.

Crystal Orientation and Brightness.

The crystallites in normal nickel or in the electro-deposited metal after annealing are arranged at random. Under the directive influence of the field of force in the electrolyte the grains tend to grow with a given crystallographic axis in the same direction. This is known to result in variations of the relative intensity of the diffraction lines ; in the experimental dispositions usually employed maxima and minima of intensity are produced along the length of the lines. A measure of the degree of the orientation is provided by the ratio of intensity of a point on a line where a maximum forms to that of a point which tends to a minimum. It is convenient to choose a maximum on one line and a minimum actually on a second line so that each point falls where the lines cross the equatorial line of the diffraction photograph. In the present work the (111) and (200) lines were found to give a suitable indication. The intensity of the lines at the points indicated was obtained with the aid of a Moll microphotometer, and the ratio of the heights of the peaks above the continuous background of the microphotometer record was taken as a measure of the orientation. The peaks varied from cases in which the (111) was stronger than the (200), the normal ratio for a random crystallographic orientation, to cases where the (111) was weaker.

The specimens were grouped in this way into sets in which the ratio of the (111) to the (200) peak was greater than or less than unity. It was then found that the bright type of deposit fell into the second set in every case examined; this type therefore appeared to be associated with a highly oriented structure. The randomly oriented deposits showed the dull grey appearance. The observations for a typical set of specimens are summarized in Table I.

The results were extended to approximately fifty specimens, and consistently showed a correspondence between the state of crystalline orientation and the lustre of the

TABLE I.

Specimen.	Current density (m.amp./cm. ²).	Electrode potential (volts).	Plating bath.	Ratio of (111) to (200) line.	Nature of deposit.
<i>a</i>	4	2.2	2	< 1	Bright.
<i>b</i>	5	2.5	..	= 1	Bright.
<i>c</i>	20	2.8	..	< 1	Bright.
<i>d</i>	30	2.9	..	> 1	Dull.
<i>e</i>	40	3.2	..	> 1	Dull.
<i>f</i>	50	3.4	..	> 1	Dull.
<i>g</i>	5	0.75	1	< 1	Bright.
<i>h</i>	10	0.8	..	< 1	Bright.
<i>i</i>	20	1.5	..	> 1	Dull.
<i>j</i>	50	2.2	..	> 1	Dull.

deposit as taken from the bath. In general the orientation was greater for the lesser current densities, and decreased as the current increased. This would suggest that at the slower rates of deposition the various grains are given time to grow in the same way, and a preferred direction of orientation, once started, could be maintained. At the higher current densities, however, different grains would grow under more rapid and disturbed conditions, and would tend to produce a less regular surface, giving diffuse reflexion of light and imparting a dull appearance. Similar results showing a connexion between degree of orientation and initial lustre were found to characterize electro-deposited chromium coatings.

No consistent relation, on the other hand, could be traced between the degree of orientation and the hardness.

In this matter the present results are somewhat at variance with those of other workers ⁽²⁾; but the inference is to be anticipated from work on the strain-hardening produced in metals by cold-work. It has been shown by the author that the selective orientation produced as a metal is severely cold-worked appears and grows after the main modifications in hardness have taken place ⁽³⁾, and that therefore the selective orientation caused by cold-deformation cannot be a primary factor responsible for strain-hardening; but in the same experiments it was found that the hardening appeared to be associated with the diffusion of the X-ray spectral lines ⁽⁴⁾. A neglect of the aspect of the X-ray photographs probably accounts for the discrepancies referred to above. The spectra of the deposits were examined further from this point of view.

Breadth of Spectral Lines and Hardness.

The breadth of the spectral lines, obtained with the aid of iron $K\alpha$ radiation, varied from cases in which the α_1 and α_2 components of the (311) line were sharply separated to others in which the components diffused into each other and formed a single band. The (311) line occurred at the diffraction angle $\theta = 66^\circ.3$, and was therefore sufficiently sensitive to changes in resolution to afford a basis for quantitative measurements. Each specimen was photographed under exactly the same conditions in a precision camera giving high resolution, and a microphotometer record taken of the (311) line. The breadth of the line at the points on the peaks where the intensity is one-half of the maximum was measured. A standard spectrum was then obtained from a specimen of nickel plate which had been annealed sufficiently to free the crystal lattice from distortion and to increase the grain size to the range of values giving sharply resolved spectrum lines. The breadth of the (311) line given by this specimen was taken as the minimum value obtainable with the experimental arrangements employed. The difference between the standard breadth thus obtained and that given by the microphotometer records of the various electroplated specimens was secured by subtraction, and since the conditions of experiment were the same throughout any increases in breadth could be taken

as a measure of the associated changes of structure in the specimens.

This value of the line breadth includes the additive effect of the α_1 and α_2 components of the line. It can be corrected to give the breadth due to the α_1 component by applying the following formula deduced by Brill ⁽⁵⁾ :

$$b = \frac{B}{2} \left\{ 1 + \sqrt{1 - \frac{4\delta}{3B}} \right\},$$

where B is the measured and b the corrected breadth, and δ the separation of the doublet. It was found in practice that the procedure of finding the increase in line-breadth over the standard minimum by subtraction automatically allowed for the effect of the α_2 component within the limits of experimental error.

When the increments in breadth of the (311) line in the spectra of the various specimens were compared with the hardness, a marked association between the two factors became evident ; the greater the hardness of the nickel coating over the normal metal the greater the breadth of the spectral lines. In general the harder deposits were given by the nickel ammonium sulphate type of bath, formula (2), and these deposits gave the broader spectral lines. The softest deposit was obtained at a low current density from the nickel sulphate bath, formula (1), and the spectrum of this deposit was the only one to show good resolution of the $\alpha_1 \alpha_2$ doublet components of the (311) line.

A series of deposits on which accurate hardness measurements were made in the Engineering Department, National Physical Laboratory, gave the results shown in Table II. The hardness numbers are given in terms of the measurements of test compressions by a 136° diamond pyramid, with a load of 2 kgm. for the thicker deposits and 10 gm. for the thinner ones, using the tables of Diamond Pyramid Hardness, Brit. Standard Spec. No. 427, 1931. The increases in line-breadth, δx , are as read from the bromide paper record of the Moll microphotometer, and are given in millimetres so as to indicate the magnitudes actually involved in measuring the broadening of the line ; the value of δx may be reduced to the angular breadth of line subtended at the centre of the circular camera employed by the relation

$$\delta\theta = 0.0026 \times \delta x,$$

which takes into account the magnification introduced by the gearing of the recording drum of the microphotometer and the dimensions of the X-ray camera.

The above results confirm an association between the broadening of the spectral lines and the hardness of a metal which has been suggested by previous work on the spectra of cold-rolled metals, tungsten magnet steels, and nitrified steels.

TABLE II.

Specimen.	Current density (m.amp./cm. ²).	Bath.	Increase in line breadth over standard (mm.).	Hardness (D.P.H.).
1	5	1	2.0	182
2	40	1	4.0	230
3	30	1	4.0	241
4	10	1	6.0	301
5	15	1	6.0	310
6	50	2	7.0	362
7	60	2	8.5	431

Interpretation of the Line-broadening.

A final explanation of the broadening in terms of the structure of the metal cannot, in the present state of the subject, be given, because the effect may be due to a combination of two factors—fine-grain and lattice-distortion. The following points, however, are noted :—

(1) In the case of electro-deposited metals the existence of line-broadening in the spectrum has been attributed invariably by other workers to the very small size of the crystallites; the broadening begins as the number of atomic planes in the average crystallite becomes less than that required for adequate resolution. This occurs when the size of the crystallite is reduced to the order of 10^{-5} cm. Then the change in the angular range subtended by the half-breadth of the line is given by Scherrer's formula ⁽⁶⁾

$$\delta B = \frac{0.9 \lambda}{s \cos \theta},$$

where λ is the wave-length used, s the mean linear size of the crystallite, and θ the angle of diffraction of the line.

Applying the relation to the measurements made on specimens 1 to 7 we have the values of the crystallite size given in Table III.

Using this interpretation of the line-broadening we find that the softest nickel deposits are composed of crystallites of the order of 10^{-5} cm. in size, and the hardest of crystallites reduced in size to approximately 10^{-6} cm.; and that the hardness is associated with the state of the crystalline structure of the metal when existing in this subnormal crystallite size. It should be pointed out that the crystallites observed by the X-ray method are not necessarily the same as the grains observed by the metallurgical method of polishing and etching; the crystallites may be components of the mosaic which constitutes a

TABLE III.

Specimen.	Hardness.	Grain size required to produce broadening observed.
1	182	8.4×10^{-5} cm.
2	230	4.2
3	241	4.2
4	301	2.8
5	310	2.8
6	362	2.4
7	431	2.0

metallurgical grain, for they can behave as independently reflecting units to an X-ray beam before they differ sufficiently amongst themselves in crystallographic orientation to produce separate grain boundaries in microscopic examination.

(2) The line-broadening which occurs in the spectrum of a metal subjected to deformation by cold-work is attributed to distortion of the crystal-lattice; this broadening increases rapidly in the early stages of working and then tends to a maximum characteristic of the metal. It is of interest to compare this maximum for cold-worked nickel with the observations on the metal when electro-deposited. Measured under the same conditions as the latter and expressed in the form used in Table II. the value of the maximum has been found to be 6 mm. The breadth of the same line in the spectra of specimens

6 and 7, as shown in Table II., exceeds that value by 1 and 2.5 mm. respectively. In the case of these specimens therefore the line broadening cannot be due to lattice-distortion only; consequently this observation shows, for the first time, that this factor cannot alone be responsible for the increase in hardness which a metal can be made to exhibit.

In conclusion, the author's thanks are due to Dr. G. W. C. Kaye for his interest in the researches of which the above is part, and to Mr. J. A. G. Smith for efficient help in the technical details of the work.

Summary.

An X-ray diffraction examination has been made of specimens of electro-deposited nickel differing in hardness and initial brightness. The brightness has been found to be associated with the degree of selective orientation of the metal grains, and the hardness with the degree of diffusion of the X-ray diffraction spectra. The diffusion of the lines has been discussed in terms of fine-grain and lattice-distortion, and the grain size has been estimated from the broadening of the spectral lines for a series of deposits of known hardness values.

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LXXXVI. *Some Applications of Whittaker's Extension of Gauss's Theorem in General Relativity.* By J. T. COMBRIDGE, M.A., *University of London, King's College* *.

1. **T**HE pure mathematical difficulties in the way of obtaining solutions of Einstein's gravitational equations have hitherto been followed by a difficulty in the domain of applied mathematics. When a solution

* Communicated by the Author.

of these equations has been found it is desirable to discover to what distribution of matter this solution corresponds. The method of investigation has usually been to obtain the equations of the geodesics of the Riemannian space determined by the solution of the gravitational equations, and to compare the constants in them with those in the Newtonian equations of motion to which these geodesic equations appear analogous. A slightly more systematic procedure is to find the components of the initial acceleration of a test particle placed at rest (relative to an observer at the origin of coordinates) at various points of the field.

Professor Whittaker has now* given a method for finding the total mass in a given region giving rise to an assigned gravitational field represented by a quadratic differential form, or line-element, whose coefficients satisfy Einstein's gravitational equations. Moreover, when the gravitational field is not due entirely to matter, Whittaker's method gives the volume integral of the so-called energy tensor over a given region of space. An extension of Gauss's Theorem for the electrostatic potential is also indicated in the same paper.

As an interesting confirmation of results obtained by the older methods, and of the applicability of Whittaker's methods, we here apply the latter to three existing solutions of Einstein's equations, namely:

- (a) Wilson's solution for the field of an infinite rod †.
- (b) Curzon's solution for the field of two particles (kept apart by suitable constraints) ‡.
- (c) Jeffery's solution for the field of an electron §.

With regard to (a) and (b), solutions corresponding to fields possessing axial symmetry had been given previously by Weyl|| and Levi-Civita ¶, while the field of an electron had been given by Nordström **. The particular and independent derivations by the English authors quoted are, however, performed by methods more familiar to English readers, and in the first two cases the forms

* Proc. Roy. Soc. (A) cxlix. p. 384 (1935).

† Phil. Mag. (ser. 6) xl. p. 703 (1920).

‡ Proc. Lond. Math. Soc. xxiii. pp. xxix and 477 (1924-5).

§ Proc. Roy. Soc. (A) xcix. p. 123 (1921).

|| *Ann. der Phys.* liv. p. 117 (1917).

¶ *Rend. R. Accad. dei Lincei* (ser. 5) 28 i. pp. 4 & 101 (1919).

** Proc. Amst. Acad. xx. p. 1236 (1918).

of the results lend themselves more readily to our present purpose. We may perhaps remark that the mass with which these writers identify certain constants in their results is the gravitational mass of the source of the field obtained; Whittaker's work implies equality of the gravitational and the inertial mass of the source—an equality already well established by other reasoning.

2. *Wilson's Solution*.—The line-element is

$$ds^2 = c^2 r^{4m/(1-2m)} dt^2 - r^{8m/(1-2m)} dr^2 - r^{4m} dz^2 - r^2 d\phi^2, \quad (1)$$

where r, z, ϕ are spatial cylindrical polar coordinates and m is a constant of integration. Comparing this with Whittaker's standard form * $d\tau^2$ (where $d\tau^2 = ds^2/c^2$),

$$d\tau^2 = U dt^2 - \frac{1}{c^2} \sum_{i,k} a_{ik} dx_i dx_k, \quad (i, k=1, 2, 3). \quad (2)$$

we see that we have to take $U = r^{4m/(1-2m)}$. Whittaker's condition of normalization—that is, that $U \rightarrow 1$ as $r \rightarrow \infty$ —confronts us with the same difficulty as is experienced in Newtonian potential theory in dealing with the potential of an infinite rod. The condition proves, however, to be of no significance for us here, and may be ignored.

We have to evaluate over an arbitrary simple closed surface

$$-c^3 \iint \sum_1^3 \left\{ g^1 \frac{\partial(x_2, x_3)}{\partial(u, v)} \right\} \sqrt{-g} du dv, \quad (3)$$

where

$$g^i = -\frac{1}{2} c^2 \sum_{k=1}^3 \frac{a^{ik}}{U} \frac{\partial U}{\partial x_k} \quad (i=1, 2, 3);$$

g is the determinant of the coefficients of the line-element (2); u, v are Gaussian coordinates on the closed surface in question; x_1, x_2, x_3 are our spatial coordinates and may be taken to be r, z, ϕ respectively. If we take as our closed surface a cylinder $r = \text{constant}$ bounded by planes $z = z_1, z = z_2$, we may put $u = z, v = \phi$. The summation in the integrand of (3) reduces to the single term containing g^1 , for g^2 and g^3 are both zero, since $a^{ik} = 0$

* As we shall only be evaluating certain expressions for particular coordinate systems, I have thought it clearer to write the coordinates with suffixes rather than to follow Whittaker in emphasizing their contravariant character by writing them with the suffixes raised. But in the case of g^i and a^{ik} the i and k denote contravariant character.

unless $k=i$, and $\partial U/\partial x_k=0$ unless $k=1$. Further, $a^{11}=1/a_{11}=r^{-8m^2/(1-2m)}$. Hence

$$g^1 = -\frac{2mc^2}{1-2m} r^{-1-8m^2/(1-2m)}; \quad \sqrt{-g} = c^{-3} r^{1-2m+2m(1+2m)/(1-2m)},$$

and so (3) reduces to

$$\frac{2mc^2}{1-2m} \int_{z_1}^{z_2} \int_0^{2\pi} d\phi dz; \quad i.e., \quad \frac{4\pi mc^2}{1-2m} \int_{z_1}^{z_2} dz.$$

It appears therefore that Whittaker's result is verified in this case provided the line-density is not m (as was previously supposed) but λ , where $\kappa\lambda=mc^2(1-2m)$, κ being the Newtonian gravitation constant. This result is in agreement with Wilson's assumption of m for the line-density to within the order of approximation employed by him in comparing his geodesic equations with the equations of motion of the corresponding Newtonian field. Two constants, m and a , appear in his solution, connected, as he shows, by the relation $a=4m/(1-2m)$; the method of determining the mass by the geodesic equations does not enable us to distinguish between them. As a matter of fact Kasner* gave a symmetrical solution of this type in 1921 (but without interpretation), namely,

$$ds^2 = x_1^{2a_1} dx_1^2 + x_1^{2a_2} dx_2^2 + x_1^{2a_3} dx_3^2 + x_1^{2a_4} dx_4^2,$$

where the a 's are constants of integration satisfying the conditions

$$\begin{aligned} a_2 + a_3 + a_4 &= 0, \\ a_2^2 + a_3^2 + a_4^2 &= (a_1 + 1)^2. \end{aligned}$$

The particular values

$$a_1 = \frac{4m^2}{1-2m}, \quad a_2 = -2m, \quad a_3 = 1, \quad a_4 = \frac{2m}{1-2m}$$

(which are consistent with the above conditions), together with appropriate change of variables, give Wilson's solution.

3. *Curzon's Solution*.—The line-element is

$$ds^2 = -e^\lambda(dx_1^2 + dx_2^2) - x_2^2 e^{-\rho} d\phi^2 + c^2 e^\rho dt^2, \quad (4)$$

* Amer. Journ. Math. xliii. p. 217 (1921).

where

$$\lambda = \frac{2m_1}{r_1} + \frac{2m_2}{r_2} - \frac{m_1^2}{r_1^2} \sin^2 \theta_1 - \frac{2m_1 m_2}{a^2} \sin^2 \frac{\theta_1 - \theta_2}{2} - \frac{m_2^2}{r_2^2} \sin^2 \theta_2 ;$$

$$\rho = -\frac{2m_1}{r_1} - \frac{2m_2}{r_2} ; \quad r_1^2 = (x_1 - a)^2 + x_2^2 ; \quad r_2^2 = (x_1 + a)^2 + x_2^2 ;$$

the axis of x_1 (instead of x_2) being now the axis of symmetry. The form $d\tau^2 (=ds^2/c^2)$ is normalized, since $U=e^\rho \rightarrow 1$ as $x_2 \rightarrow \infty$. Since U is a function of x_1 and x_2 only, and $a^{12}=0$,

$$g^1 = -\frac{1}{2} c^2 a^{11} \frac{\partial \rho}{\partial x_1} = -c^2 e^{-\lambda} \{m_1(x_1 - a)/r_1^3 + m_2(x_1 + a)/r_2^3\},$$

$$g^2 = -\frac{1}{2} c^2 a^{22} \frac{\partial \rho}{\partial x_2} = -c^2 e^{-\lambda} \{m_1 x_2 / r_1^3 + m_2 x_2 / r_2^3\}, \quad g^3 = 0.$$

Also $\sqrt{-g} = c^{-3} x_2 e^\lambda$. Let us take as our closed surface the cylinder of radius R and length $2a$ having its axis along the axis of symmetry and its centre at the point $(a, 0, 0)$. The integral (3) then falls into three parts :

$$\begin{aligned} I_1 &= -c^3 \iint g^2 \sqrt{-g} dx_1 d\phi \text{ (over the curved surface)} \\ &= 2\pi c^2 \int_0^{2a} \left\{ \frac{m_1 R^2}{[(x_1 - a)^2 + R^2]^{3/2}} + \frac{m_2 R^2}{[(x_1 + a)^2 + R^2]^{3/2}} \right\} dx_1, \end{aligned}$$

$$\begin{aligned} I_2 &= -c^3 \iint g^1 \sqrt{-g} dx_2 d\phi \text{ (over the plane end } x_1 = 2a) \\ &= 2\pi c^2 \int_0^R \left\{ \frac{m_1 a x_2}{(a^2 + x_2^2)^{3/2}} + \frac{3m_2 a x_2}{(9a^2 + x_2^2)^{3/2}} \right\} dx_2, \end{aligned}$$

$$\begin{aligned} I_3 &= c^3 \iint g^1 \sqrt{-g} dx_2 d\phi \text{ (over the plane end } x_1 = 0) \\ &= 2\pi c^2 \int_0^R \left\{ \frac{m_1 a x_2}{(a^2 + x_2^2)^{3/2}} - \frac{m_2 a x_2}{(a^2 + x_2^2)^{3/2}} \right\} dx_2. \end{aligned}$$

Evaluating these definite integrals, and summing, we find eventually

$$I_1 + I_2 + I_3 = 4\pi c^2 m_1,$$

so that Whittaker's method gives the mass enclosed in this cylinder as $\kappa m_1 / c^2$. Similarly it could be shown that the singularity at $(-a, 0, 0)$ is due to a mass $\kappa m_2 / c^2$.

4. *The Nordström-Jeffery Solution.*—The line-element involves both the mass of the electron and its charge. Application of the same extension of Gauss's Theorem as that used in the two preceding sections gives not only the material mass but also the mass corresponding to the electrostatic energy. Application of Whittaker's extension of Gauss's electrostatic theorem gives the charge of the electron.

The line-element is

$$ds^2 = c^2 \gamma dt^2 - \gamma^{-1} dr^2 - r^2 d\theta^2 - r^2 \sin^2 \theta d\phi^2, \quad . \quad . \quad (5)$$

where

$$\gamma = 1 - \frac{2\kappa m}{c^2 r} + \frac{\kappa \epsilon^2}{4\pi c^4 r^2},$$

m being the mass of the electron, ϵ its charge in Lorentz units, κ the Newtonian gravitation constant, and c the speed of light. As before, we consider $d\tau^2 = ds^2/c^2$; we then put $r = x_1$, $\theta = x_2 = u$, and $\phi = x_3 = v$, and take as our closed surface a sphere $r = R$ (a constant). The integral (3) then reduces to

$$-c^3 \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \int_0^{2\pi} g^1 \sqrt{-g} d\phi d\theta,$$

where

$$\sqrt{-g} = c^{-3} r^2 \sin \theta,$$

and

$$g^1 = -\frac{1}{2} c^2 \frac{a^{11}}{U} \frac{dU}{dr},$$

with $a^{11} = \gamma = U$ and $\frac{dU}{dr} = \frac{2\kappa m}{c^2 r^2} - \frac{\kappa \epsilon^2}{2\pi c^4 r^3}.$

The integral is therefore

$$\frac{1}{2} c^2 \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \int_0^{2\pi} \left(\frac{2\kappa m}{c^2} - \frac{\kappa \epsilon^2}{2\pi c^4 R} \right) \sin \theta d\phi d\theta,$$

which, when evaluated, gives

$$4\pi\kappa \left(m - \frac{\epsilon^2}{4\pi c^2 R} \right).$$

If e is the charge in electrostatic units and W the electrostatic energy inside the sphere of radius R , $\epsilon^2 = 4\pi e^2$

and $W = -e^2/R$; the total mass inside this sphere is therefore given by this theorem as

$$m + W/c^2.$$

To apply the extension of Gauss's electrostatic theorem we have to evaluate

$$\iint \left\{ X^{23} \frac{\partial (x_0, x_1)}{\partial (u, v)} + \dots + \dots \right. \\ \left. + X^{01} \frac{\partial (x_2, x_3)}{\partial (u, v)} + \dots + \dots \right\} \sqrt{-g} \, du \, dv, \quad (6)$$

where the index 0 indicates the time and X^{ik} is the six-vector of which three components represent the electric, and the other three the magnetic force vector. In our present case the only surviving component is X^{01} (the F^{14} of Jeffery's paper), which is equal to $\epsilon/(4\pi r^2)$. The integral (6) therefore reduces to

$$\int_0^{2\pi} \int_{-\frac{\pi}{2}}^{\frac{\pi}{2}} \frac{\epsilon}{4\pi r^2} \cdot r^2 \sin \theta \, d\theta \, d\phi,$$

taken over the sphere $r=R$, and thus gives the total charge inside this sphere, provided the quantity $\sqrt{-g}$ be given the value it has in Jeffery's paper—i. e., *provided it be calculated on the basis of the line-element*

$$ds^2 = \gamma \, dx_0^2 - \gamma^{-1} \, dr^2 - r^2 \, d\theta^2 - r^2 \sin^2 \theta \, d\phi^2,$$

and not on the basis of the standard form (2) in which U is normalized.

LXXVII. *A Contribution to the Symbolic Calculus.* By
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Introduction.

WITH this calculus is meant specially that of Carson and van der Pol, which, as will be known, originates from Heaviside's operational calculus. The first fundamental rules were laid down by Carson in his book 'Electric Circuit Theory and the Operational Calculus' †,

* Communicated by the Author.

† J. R. Carson, 'Electric Circuit Theory and the Operational Calculus,' chap. iv. (McGraw-Hill, New York, 1926.)

and were used there specially for solving problems relating to electrical networks. Van der Pol* extended those rules and showed their great heuristic value for discovering mathematical relations between several functions. Not only for problems in mathematics †, but also in physical problems ‡, such as the propagation of radio-waves, this calculus appeared to be very useful.

The essential point in it is that a function $h(x)$ is represented by its "image" $f(p)$, constructed in the way of a Laplace-transform :

$$f(p) = p \int_0^{\infty} e^{-px} h(x) dx, \quad . \quad . \quad . \quad (1)$$

and this representational connexion between "original" $h(x)$ and "image" $f(p)$ is indicated by

$$f(p) \doteq h(x) \quad \text{or} \quad h(x) \doteq f(p). \quad . \quad . \quad . \quad (2)$$

This correlation is in both directions one by one. For more details one is referred to the above papers in the 'Philosophical Magazine,' and for a suitable introduction to a booklet of Humbert§.

The power of the symbolic calculus will be increased by an increasing number of known relations $f(p) \doteq h(x)$, and the rules of Carson and van der Pol, mentioned above, just had in view to derive from a known pair $f(p), h(x)$ other pairs $F(p), H(x)$. So, for instance, the following new pair was derived from (1):

$$f\left(\frac{p}{a}\right) \doteq h(ax) \quad (a = \text{constant}), \quad (3)$$

and among many other ones also, *e. g.*,

$$\int_0^p \frac{f(p)}{p} dp \doteq \int_x^{\infty} \frac{h(s)}{s} ds. \quad . \quad . \quad . \quad (4)$$

But also other types were known, where the new image followed by a substitution from the old one (as, *e. g.*, in (3)), whereas the new "original" followed by means of

* Balth. van der Pol, *Phil. Mag.* viii. p. 861 (1929).

† Balth. van der Pol and K. F. Niessen, *Phil. Mag.* xiii. p. 537 (1932).

‡ Balth. van der Pol and K. F. Niessen, *Ann. der Physik.* vi. p. 273 (1930), and x. p. 485 (1931).

§ P. Humbert, "Le Calcul Symbolique" ('Actualités scientifiques et industrielles,' No. 147). (Hermann et Cie, Paris, 1934.)

an integration whose integrand contained the old original $h(x)$ (which also was the case in (4)).

These rules were: *

$$pf\left(\frac{1}{p}\right) \doteq \int_0^\infty J_0(2\sqrt{sx})h(s) ds, \quad . \quad . \quad (5)$$

$$f\left(\frac{1}{p}\right) \doteq \int_0^\infty \sqrt{\frac{x}{s}} J_1(2\sqrt{xs})h(s) ds, \quad . \quad . \quad (6)$$

$$f(\sqrt{p}) \doteq \frac{1}{\sqrt{\pi x}} \int_0^\infty e^{-\frac{x^2}{4s}} h(s) ds, \quad . \quad . \quad (7)$$

$$f\left(p + \frac{1}{p}\right) \doteq \int_0^x J_0(2\sqrt{s(x-s)})h(s) ds. \quad . \quad . \quad (8)$$

$$p + \frac{1}{p}$$

In this paper, now, we wish to increase the number of rules of the last kind and, by means of the new rules, to find out the original functions belonging to some simple images.

The use of relations of the kind of (5)–(8) for electrical networks is demonstrated by van der Pol † and Ekelöf ‡. See also J. P. Schouten § and L. Kosten ||, who use, for the interpretation of images, always Bromwich's integrals where p has, in general, a complex value, while our parameter p has to be always positive and real.

Derivation of some General Rules.

1. From (1) we form

$$\frac{1}{p^{n-1}} f\left(\frac{1}{p}\right) = \int_0^\infty \frac{s^n}{p^n} e^{-\frac{s}{p}} \frac{h(s)}{s^n} ds,$$

and then, by means of the known relation,

$$\frac{s^n}{p^n} e^{-\frac{s}{p}} \doteq (xs)^{\frac{n}{2}} J_n(2\sqrt{sx}),$$

* Balth. van der Pol and K. F. Niessen, *Phil. Mag.* xiii. p. 537 (1932).

† Balth. van der Pol, *Physica*, i. p. 521 (1934).

‡ Ekelöf, *E. N. T.* xii. p. 100 (1935).

§ J. P. Schouten, *Physica*, ii. p. 75 (1935).

|| L. Kosten, *Physica*, ii. (1935).

we obtain the general rule

$$\frac{1}{p^{n-1}} f\left(\frac{1}{p}\right) \doteq \int_0^\infty \left(\frac{x}{s}\right)^2 J_n(2\sqrt{xs}) h(s) ds, \quad (1.)$$

(n=0, 1, 2, 3...)

which, for the special cases $n=0$ and $n=1$, leads to (5) and (6).

2. From (1) we form

$$(\sqrt{p})^m f(\sqrt{p}) = \int_0^\infty (\sqrt{p})^m \sqrt{p} e^{-s\sqrt{p}} h(s) ds. \quad (9)$$

Starting from the known relation

$$\sqrt{p} e^{-s\sqrt{p}} \doteq \frac{e^{-\frac{s^2}{4x}}}{\sqrt{\pi x}}, \quad (10)$$

we obtain, by m differentiations with respect to s ,

$$(-\sqrt{p})^m \sqrt{p} e^{-s\sqrt{p}} \doteq \frac{1}{\sqrt{\pi x}} \frac{d^m}{ds^m} \left(e^{-\frac{s^2}{4x}} \right), \quad (11)$$

(m=0, 1, 2, ...)

by means of which (9) gives

$$(-\sqrt{p})^m f(\sqrt{p}) \doteq \frac{1}{\sqrt{\pi x}} \int_0^\infty h(s) \frac{d^m}{ds^m} \left(e^{-\frac{s^2}{4x}} \right) ds. \quad (12)$$

From the definition of the Hermite polynomials,

$$\text{He}_m(\xi) = (-1)^m e^{\xi^2} \frac{d^m e^{-\xi^2}}{d\xi^m},$$

it follows that

$$\frac{d^m}{ds^m} \left(e^{-\frac{s^2}{4x}} \right) = (-1)^m e^{-\frac{s^2}{4x}} \frac{1}{(2\sqrt{x})^m} \text{He}_m \left(\frac{s}{2\sqrt{x}} \right),$$

which gives, by substitution in (12),

$$(\sqrt{p})^m f(\sqrt{p}) \doteq \frac{2}{\sqrt{\pi}} \frac{1}{(2\sqrt{x})^{m+1}} \int_0^\infty h(s) e^{-\frac{s^2}{4x}} \text{He}_m \left(\frac{s}{2\sqrt{x}} \right) ds, \quad (\text{II.})$$

valid for $m=0, 1, 2, 3, \dots$

Thanks to the introduction of the Hermite functions (to which Dr. van der Pol drew my attention) the relation (12) could be brought in the elegant form of (II.).

If we had transformed the right side of (12) by means of successive partial integrations instead of introducing Hermite functions, we would have found

$$p^{n+1}f(\sqrt{p}) = \frac{1}{\sqrt{\pi x}} \int_0^\infty e^{-\frac{s^2}{4x}} h^{(2n+1)}(s) ds + \frac{1}{\sqrt{\pi x}} \sum_{i=0}^n \frac{h^{(2i)}(0)}{(-4x)^{n-i}} \frac{(2n-2i)!}{(n-i)!} \quad (\text{II. } a)$$

and

$$p^n f(\sqrt{p}) = \frac{1}{\sqrt{\pi x}} \int_0^\infty e^{-\frac{s^2}{4x}} h^{(2n)}(s) ds + \frac{1}{\sqrt{\pi x}} \sum_{i=1}^n \frac{h^{(2i-1)}(0)}{(-4x)^{n-i}} \frac{(2n-2i)!}{(n-i)!}, \quad (\text{II. } b)$$

with the abbreviation

$$h^{(m)}(s) = \frac{d^m h(s)}{ds^m}.$$

The special case $n=0$ in (II. b) leads to (7).

3. Whereas (I.), (II. a), and (II. b) were mere extensions of the known rules (5), (6), (7), we now will derive a rule of quite another character.

For this we start from the known relation

$$\frac{p}{\sqrt{p^2+1}} e^{-\sqrt{p^2+1}\xi} = \begin{cases} 0 & \text{for } x < \xi, \\ J_0(\sqrt{x^2-\xi^2}) & \text{for } x > \xi. \end{cases} \quad (13)$$

Apparently ξ is a constant, which in the "original" on the right side does not only appear in the form of the function itself, but also indicates the place of the discontinuity where the function J_0 suddenly comes into play. Therefore a differentiation with respect to ξ in the ordinary way (a mere differentiation of image- and original function, as, for instance, in (10) and (11)) is not permitted. Yet a differentiating process is possible but requires a closer examination. (Choosing, instead of ξ , the constant $\xi+d\xi$, we get

$$\frac{p}{\sqrt{p^2+1}} e^{-\sqrt{p^2+1}(\xi+d\xi)} = \begin{cases} 0 & \text{for } x < \xi+d\xi, \\ J_0(\sqrt{x^2-(\xi+d\xi)^2}) & \text{for } x > \xi+d\xi. \end{cases} \quad (14)$$

Writing (13) and (14) in the form

$$f_1(p) \doteq h_1(x), \quad f_2(p) \doteq h_2(x),$$

we may conclude

$$f_2(p) - f_1(p) \doteq h_2(x) - h_1(x),$$

the first member of which can be obtained by a mere differentiation of $f_1(p)$ with respect to p .

For the second member we divide the range $0 < x < \infty$ in three intervals :

$$-pe^{-\sqrt{p^2+1}\xi} d\xi \doteq \begin{cases} 0 & \text{for } x < \xi, \\ -1 & \text{for } \xi < x < \xi + d\xi, \\ \frac{dJ_0(\sqrt{x^2-\xi^2})}{d\xi} \cdot d\xi & \text{for } x > \xi + d\xi. \end{cases}$$

Special attention must be paid to the interval $\xi < x < \xi + d\xi$, where appeared

$$0 - J_0(\sqrt{x^2-\xi^2}) = 0 - J_0(0) = -1.$$

From (1) we have, of course,

$$af(p) \doteq ah(x),$$

a being a constant. Choosing this to be

$$a = \frac{1}{d\xi},$$

and transforming

$$\frac{dJ_0(\sqrt{x^2-\xi^2})}{d\xi} = \frac{\xi}{\sqrt{x^2-\xi^2}} J_1(\sqrt{x^2-\xi^2}),$$

we arrive at

$$-pe^{-\sqrt{p^2+1}\xi} d\xi \doteq \begin{cases} 0 & \text{for } x < \xi, \\ -\frac{1}{d\xi} & \text{for } \xi < x < \xi + d\xi, \\ \frac{\xi}{\sqrt{x^2-\xi^2}} J_1(\sqrt{x^2-\xi^2}) & \text{for } x > \xi + d\xi. \end{cases}$$

In the interval $\xi < x < \xi + d\xi$ the function on the right side becomes $-\infty$, if we take $d\xi \rightarrow 0$, but yet so that an integration from $x = \xi$ to $x = \xi + d\xi$ gives -1 .

Taking $d\xi=0$, we therefore can write, using only two intervals,

$$-pe^{-\sqrt{p^2+1}\xi} = \begin{cases} 0 & \text{for } x < \xi, \\ -2\delta(x-\xi) + \frac{\xi}{\sqrt{x^2-\xi^2}} J_1(\sqrt{x^2-\xi^2}) & \text{for } x > \xi. \end{cases}$$

. . . (15)

Here $\delta(x-\xi)$ is the impulsive function of Dirac, being $+\infty$ at $\xi=x$, but still fulfilling

$$\int_{-\infty}^{+\infty} \delta(x-\xi) d\xi = 1, \quad . \quad . \quad . \quad . \quad . \quad (16)$$

$$\int_x^\infty \delta(x-\xi) d\xi = \frac{1}{2}. \quad . \quad . \quad . \quad . \quad (17)$$

As the writer was informed, a relation equivalent to (15) had been found by Dr. van der Pol, whose derivation (unpublished) will be given below. It is of a more analytical character than the former (more geometrical) one.

Equivalent to the *symbolic* relation (13) is the *ordinary* equation

$$\frac{p}{\sqrt{p^2+1}} e^{-\xi\sqrt{p^2+1}} = p \int_\xi^\infty e^{-p\xi} J_0'(\sqrt{s^2-\xi^2}) ds.$$

Introducing

$$\sqrt{s^2-\xi^2} = v,$$

the right side of the preceding equation can be written as

$$\begin{aligned} - \int_0^\infty J_0(v) \frac{d}{dv} (e^{-p\sqrt{v^2+\xi^2}}) dv \\ = e^{-p\xi} + \int_0^\infty e^{-p\sqrt{v^2+\xi^2}} J_0'(v) dv, \end{aligned}$$

so that the equation may be brought in the form

$$\frac{p}{\sqrt{p^2+1}} e^{-\xi\sqrt{p^2+1}} - e^{-p\xi} = \int_0^\infty e^{-p\sqrt{v^2+\xi^2}} J_0'(v) dv.$$

This ordinary equation differentiated with respect to ξ gives

$$\begin{aligned} pe^{-\xi\sqrt{p^2+1}} - pe^{-p\xi} &= \int_0^\infty \frac{p\xi}{\sqrt{v^2+\xi^2}} e^{-p\sqrt{v^2+\xi}} J_0'(v) dv \\ &= p \int_\xi^\infty e^{-px} \left\{ -\frac{\partial}{\partial \xi} J_0(\sqrt{x^2-\xi^2}) \right\} dx, \end{aligned}$$

so that here an equation is obtained of the form defined by (1) and giving, therefore, a symbolic relation, namely,

$$pe^{-\xi\sqrt{p^2+1}} - pe^{-\xi p} \doteq \begin{cases} -\frac{\partial}{\partial \xi} J_0(\sqrt{x^2-\xi^2}) & \text{for } x > \xi, \\ 0 & \text{for } x < \xi. \end{cases}$$

Since $pe^{-\xi p}$ is the representation of an impulsive function at $x=\xi$,

$$pe^{-\xi p} \doteq \delta(x-\xi),$$

which may be indicated also by means of

$$pe^{-\xi p} \doteq \begin{cases} 0 & \text{for } x < \xi, \\ 2\delta(x-\xi) & \text{for } x > \xi, \end{cases}$$

the relation (15) is again obtained.

The symbolic relation (15) can now be used to interpret backwards

$$\frac{pf(\sqrt{p^2+1})}{\sqrt{p^2+1}} = \int_0^\infty pe^{-\sqrt{p^2+1}\xi} h(\xi) d\xi, \quad \dots (18)$$

constructed on the basic definition (1) of $f(p)$ and containing p only in the integrand in a factor

$$pe^{-\sqrt{p^2+1}\xi}.$$

On account of (15) the original function belonging to this factor remains zero from $x=0$ till $x=\xi$, i. e., for $x < \xi$, so that the original of (18) will be an integral over ξ with $\xi=x$ as an upper limit,

$$\begin{aligned} \frac{p}{\sqrt{p^2+1}} f(\sqrt{p^2+1}) \\ \doteq \int_0^x \left\{ 2\delta(x-\xi) - \frac{\xi}{\sqrt{x^2-\xi^2}} J_1(\sqrt{x^2-\xi^2}) \right\} h(\xi) d\xi, \end{aligned}$$

and by means of (17) we get the new general rule

$$\left. \begin{aligned} & \frac{1}{\sqrt{p^2+1}} f(\sqrt{p^2+1}) \\ & \quad = h(x) - \int_0^x h(\xi) \frac{\xi}{\sqrt{x^2-\xi^2}} J_1(\sqrt{x^2-\xi^2}) d\xi \\ & \quad = h(x) - \int_0^x h(\sqrt{x^2-s^2}) J_1(s) ds. \end{aligned} \right\} \quad (\text{III.})$$

Interpretation of some Images.

The rules (I.), (II. a), (II. b), (III.), proved above, can be used to increase the number of rules still further, for they can be applied successively in an arbitrary order, each upon the result of the foregoing one. When we would use these rules two, three, ... times in a combined manner, we would get, of course, images of a rather simple form, when expressed in f , but the corresponding original functions would look rather complicated, containing a double or threefold, ... integration. But a suitable choice of $f(p)$ and $h(x)$ in these relations with a double integral can lead to new and simple symbolic relations, where only one single integral appears in the form of the original function.

A few examples may illustrate this.

Applying rule (III.) and then still upon its result rule (I.), we obtain

$$\left. \begin{aligned} & \frac{1}{p^{n-1}} \frac{f(\sqrt{\frac{1}{p^2}+1})}{\sqrt{\frac{1}{p^2}+1}} = \frac{1}{p^{n-1}} \frac{f(\frac{\sqrt{p^2+1}}{p})}{\sqrt{p^2+1}} \\ & \quad = \int_{s=0}^{s=\infty} \left(\frac{x}{s}\right)^{\frac{n}{2}} J_n(2\sqrt{xs}) \\ & \quad \times \left[h(s) - \int_0^s h(\xi) \frac{\xi}{\sqrt{s^2-\xi^2}} J_1(\sqrt{s^2-\xi^2}) d\xi \right] ds. \end{aligned} \right\} \quad (19)$$

In order to get a simple relation, we choose

$$h(s) = \delta(s-\sigma), \quad h(\xi) = \delta(\xi-\sigma),$$

σ being a positive constant ($\sigma > 0$), so that

$$\int_0^s h(\xi) \frac{\xi}{\sqrt{s^2 - \xi^2}} J_1(\sqrt{s^2 - \xi^2}) d\xi = \begin{cases} 0 & \text{for } s < \sigma, \\ \frac{\sigma}{\sqrt{s^2 - \sigma^2}} J_1(\sqrt{s^2 - \sigma^2}) & \text{for } s > \sigma, \end{cases} \quad (20)$$

the value in the last interval on account of (16), so that the double integral in the original in (19) becomes a single one.

Together with the choice

$$h(x) = \delta(x - \sigma)$$

we are obliged, in consequence of (1), to take

$$f(p) = p e^{-p\sigma},$$

in which case the image of (19) also takes a simple explicit form. We reach in such a way the new and simple relation

$$\frac{1}{p^n} e^{-\frac{\sqrt{p^2+1}\sigma}{p}} = \left(\frac{x}{\sigma}\right)^n J_n(2\sqrt{x\sigma}) - \sigma \int_{\sigma}^{\infty} \left(\frac{x}{s}\right)^n \frac{J_n(2\sqrt{xs}) J_1(\sqrt{s^2 - \sigma^2})}{\sqrt{s^2 - \sigma^2}} ds. \quad (21)$$

Instead of applying successively (III.) and (I.) we could have taken also (III.) and (II. a), or combined (III.) with (II. b). In order to avoid inconvenient terms such as $h(o)$, $h'(o)$, etc., we will use (III.) and (II. b) with $n=0$, i. e. (III.) and (7), giving

$$\frac{\sqrt{pf(\sqrt{p^2+1})}}{\sqrt{p^2+1}} = \frac{1}{\sqrt{\pi x}} \int_{s=0}^{s=\infty} e^{-\frac{s^2}{4x}} \left[h(s) - \int_0^s h(\xi) \frac{\xi}{\sqrt{s^2 - \xi^2}} J_1(\sqrt{s^2 - \xi^2}) d\xi \right] ds. \quad (22)$$

Choosing, again,

$$h(x) = \delta(x - \sigma),$$

$$f(p) = p e^{-p\sigma},$$

which enables us to use again (20), we arrive at another new and simple symbolic relation :

$$\sqrt{p} e^{-\sqrt{p+1}\sigma} \doteq \frac{1}{\sqrt{\pi x}} e^{-\frac{\sigma}{4x}} - \frac{\sigma}{\sqrt{\pi x}} \int_{\sigma}^{\infty} e^{-\frac{s^2}{4x}} \frac{J_1(\sqrt{s^2 - \sigma^2})}{\sqrt{s^2 - \sigma^2}} ds. \quad (23)$$

Just as well the rules (I.) and (II. a) or (I.) and (II. b) could have been combined and their results simplified again by the choice $h(s) = \delta(s - \sigma)$.

We will combine, *e. g.*, the rules for

$$\frac{1}{p^{n-1}} f\left(\frac{1}{p}\right) \quad \text{and} \quad f(\sqrt{p}),$$

i. e. (I.) and (7),

$$f_1(p) = \frac{1}{p^{n-1}} f\left(\frac{1}{p}\right) \doteq \int_{\xi=0}^{\xi=\infty} \left(\frac{x}{\xi}\right)^2 J_n(2\sqrt{x\xi}) h(\xi) d\xi = h_1(x),$$

$$f_2(p) = f_1(\sqrt{p}) \doteq \frac{1}{\sqrt{\pi x}} \int_{s=0}^{s=\infty} e^{-\frac{s^2}{4x}} h_1(s) ds.$$

Therefore,

$$\frac{1}{p^{\frac{n-1}{2}}} f\left(\frac{1}{\sqrt{p}}\right) \doteq \frac{1}{\sqrt{\pi x}} \int_{s=0}^{s=\infty} e^{-\frac{s^2}{4x}} s^2 \int_{\xi=0}^{\xi=\infty} J_n(2\sqrt{s\xi}) \frac{h(\xi)}{\xi^2} d\xi ds. \quad (24)$$

In order to get a single integral we choose again,

$$h(\xi) = \delta(\xi - \sigma)$$

and correspondingly,

$$f(p) = p e^{-p\sigma},$$

for which (24) gives the simple result

$$\frac{1}{p^{\frac{n}{2}}} e^{-\frac{\sigma}{\sqrt{p}}} \doteq \frac{1}{\sigma^{n+1}} \frac{1}{\sqrt{\pi x}} \int_0^{\infty} e^{-\frac{t^2}{4\sigma^2 x}} t^{\frac{n}{2}} J_n(2\sqrt{t}) dt. \quad (25)$$

Applications.

In the above examples we always took $h(\xi) = \delta(\xi - \sigma)$ in order to reduce the double integral into a single one, but we remark that sometimes also other functions for $h(\xi)$

can be used for the same purpose. One has only to keep in mind that in (19) and (22)

$$\int_0^s h(\xi) \frac{\xi}{\sqrt{s^2 - \xi^2}} J_1(\sqrt{s^2 - \xi^2}) d\xi,$$

or in (24)

$$\int_0^\infty J_n(2\sqrt{s\xi}) \frac{h(\xi)}{\xi^{\frac{n}{2}}} d\xi, \quad \dots \quad (26)$$

has to be a known function of s , but still such a function that the integral with respect to s in (19), (22) respectively, (24) does not diverge. At the same time, of course, it is necessary that $h(\xi)$ does not contain s , since otherwise $f(p)$ would contain s , which would be in conflict with the right side of these relations, where s disappeared by the integration*.

Without going into details we may remark that a successive application of the rules (I.), (II. a), (II. b), (III.),

* For the choice of $h(\xi)$ in (26) we could, for instance, apply the known integral,

$$\int_0^\infty J_n(t) \frac{dt}{t} = \frac{1}{n},$$

whence

$$\int_0^\infty J_n(2\sqrt{s\xi}) \frac{d\xi}{\xi} = \frac{2}{n},$$

so that a suitable choice will be

$$h(\xi) = \xi^{\frac{n}{2}-1}, \quad f(p) = \frac{\Pi\left(\frac{n}{2}-1\right)}{p^{\frac{n}{2}-1}}.$$

Now the remaining single s -integral appears to be solvable too, for (24) now gives

$$\frac{\Pi\left(\frac{n}{2}-1\right)}{(\sqrt{p})^{\frac{n}{2}}} = \frac{1}{\sqrt{\pi x}} \int_0^\infty e^{-\frac{s^2}{4x}} \frac{s^{\frac{n}{2}-2}}{n} ds = \frac{2^{\frac{n}{2}+1}}{n\sqrt{\pi}} x^{\frac{n}{4}} \Pi\left(\frac{n}{4}-\frac{1}{2}\right).$$

Using the known elementary relation,

$$\frac{1}{(\sqrt{p})^{\frac{n}{2}}} = \frac{x^{\frac{n}{4}}}{\Pi\left(\frac{n}{4}\right)},$$

and the fact that the original function is defined unambiguously by the image, we find the well-known relation,

$$2^{2m} \Pi(m) \Pi\left(m-\frac{1}{2}\right) = \sqrt{\pi} \Pi(2m).$$

in an arbitrary order and taken with equal or different values $n=n_1, n=n_2, \dots$ for the integer can give us the originals, belonging to images, which have as a typical factor (besides some integer or fractional, positive, or negative power of p)

$$e^{-\sqrt{p^2+1}x}, \quad e^{-\sqrt{p+1}x}, \quad e^{-\sqrt{\sqrt{p+1}x}}, \text{ etc.} \\ e^{-\sqrt{\frac{1}{p^2+1}x}}, \quad e^{-\sqrt{\frac{1}{p+1}x}}, \quad e^{-\sqrt{\frac{1}{\sqrt{p+1}x}}}, \text{ etc.}$$

The number of possibilities is very large, but it is clear that the form of the "original" will become rather complicated by an arbitrary choice $n=n_1, n_2, \dots$ of the indices n to be used. But in practice one will be led for the choice of these indices by the wish to get finally a representation

$$F(p) \doteq H(x),$$

where some rule of Carson or of van der Pol gives a simple result. For instance, we may wish to apply the equation

$$F(\infty) = H(0), \quad . \quad . \quad . \quad . \quad . \quad (27)$$

which is well known and very powerful in the symbolic calculus. Then we have to take care that this equation will not lead to $0=0$ or $\infty=\infty$.

Another guide for the choice of rules and indices may be another fruitful equation,

$$\int_0^\infty \frac{F(p)}{p} dp = \int_0^\infty \frac{H(x)}{x} dx, \quad . \quad . \quad . \quad . \quad (28)$$

which only by a suitable choice of indices will give finite results.

A few examples may illustrate this idea.

The left-hand side of (21) is finite only for $n=0$, giving by means of (27)

$$\int_0^\infty \frac{J_1(t)}{\sqrt{t^2+\sigma^2}} dt = \frac{1-e^{-\sigma}}{\sigma}.$$

If we apply the relation (28) to (21), we obtain

$$\int_0^\infty e^{-\frac{\sqrt{p^2+1}}{p}\sigma} dp = \int_0^\infty \left(\frac{x}{\sigma}\right)^2 J_n(2\sqrt{x\sigma}) \frac{dx}{x} \\ - \sigma \int_{s=\sigma}^{s=\infty} \frac{J_1(\sqrt{s^2-\sigma^2})}{s^{\frac{n}{2}}\sqrt{s^2-\sigma^2}} \int_{x=0}^{x=\infty} x^2 J_n(2\sqrt{x\bar{s}}) \frac{dx}{x} d\bar{s}. \quad (29)$$

The index n must be chosen so that the last integral in (29) becomes finite. This integral, being also

$$2^{1-n} s^{-\frac{n}{2}} \int_0^\infty J_n(y) y^{n-1} dy,$$

is a special case of the known one

$$\int_0^\infty \frac{J_\nu(x)}{x^{\nu-2k+1}} dx = \frac{\Gamma(k-1)}{2^{\nu-2k+1} \Gamma(\nu-k)} \left[\begin{array}{l} \nu > -\frac{3}{2} \\ 0 < k < \frac{\nu}{2} + \frac{3}{4} \end{array} \right].$$

According to the conditions for ν and k we only can take $\nu=k=n=1$, obtaining then from (29) with $n=1$,

$$\int_0^\infty \frac{J_1(t) dt}{t^2 + \sigma^2} = \frac{1}{\sigma^2} - \frac{1}{\sigma^2} \int_\sigma^\infty \frac{e^{-u} u}{\sqrt{u^2 - \sigma^2}} du.$$

Some interesting results may be obtained if we combine (I.) with (II.) (the last one containing Hermite polynomials).

If we apply to

$$f(p) \doteq h(x),$$

first (I.) and then to its result rule (II.), we get

$$\begin{aligned} (\sqrt{p})^{m-n+1} f\left(\frac{1}{\sqrt{p}}\right) &\doteq \frac{2}{\sqrt{\pi}} \frac{1}{(2\sqrt{x})^{m+1}} \int_{s=0}^{s=\infty} e^{-\frac{s^2}{4x}} \text{He}_n\left(\frac{s}{2\sqrt{x}}\right) \\ &\times \int_{\xi=0}^{\xi=\infty} \left(\frac{s}{\xi}\right)^{\frac{n}{2}} J_n(2\sqrt{s\xi}) h(\xi) d\xi ds. \quad (30) \end{aligned}$$

Choosing again $h(\xi)$ and $f(p)$, as above, we arrive at

$$\begin{aligned} (\sqrt{p})^{m-n} e^{-\frac{\sigma}{\sqrt{p}}} &\doteq \frac{2}{\sqrt{\pi}} \frac{1}{(2\sqrt{x})^{m+1}} \\ &\times \int_{s=0}^{s=\infty} e^{-\frac{s^2}{4x}} \text{He}_n\left(\frac{s}{2\sqrt{x}}\right) \left(\frac{s}{\sigma}\right)^{\frac{n}{2}} J_n(2\sqrt{s\sigma}) ds. \quad (31) \end{aligned}$$

If we take

$$m=m_1, \quad n=n_1,$$

and again

$$m=m_2, \quad n=n_2,$$

but so that

$$m_1 - n_1 = m_2 - n_2,$$

the right sides of (30) and (31) must be identical, for they belong to the same image.

Or, more general, if we take

$$m=n+r,$$

r being a positive integral number (including 0), remaining constant, and n a positive but varying integral number. ($n=0, 1, 2, 3, \dots$) the right side must be independent of n .

This remark leads, after some obvious transformations, to the relation,

$$\begin{aligned} \int_0^{\sigma} e^{-u^2} u^{\frac{n}{2}} J_n(2\sqrt{yu}) \text{He}_{n+r}(u) du \\ = y^{\frac{n}{2}} \int_0^{\infty} e^{-u^2} J_0(2\sqrt{yu}) \text{He}_r(u) du. \end{aligned} \quad (32)$$

As special cases we may choose here, *e. g.*, $r=0$, $r=1$, etc., using

$$\text{He}_0(\xi)=1, \quad \text{He}_1(\xi)=2\xi,$$

giving, after some transformations,

$$\begin{aligned} \int_0^{\sigma} e^{-z^2 w^2} w^{\frac{n}{2}} J_n(2z\sqrt{w}) \text{He}_n(zw) dw \\ = \int_0^{\infty} e^{-z^2 w^2} J_0(2z\sqrt{w}) dw, \\ \int_0^{\sigma} e^{-z^2 w^2} w^{\frac{n}{2}} J_n(2z\sqrt{w}) \text{He}_{n+1}(zw) dw \\ = 2z \int_0^{\infty} e^{-z^2 w^2} J_0(2z\sqrt{w}) w dw. \end{aligned}$$

If in the combination (I.), (II.) we first had used (II.) then (I.) (*i. e.*, in a direction the reverse of that used in the foregoing) we would have found the interpretation of

$$\frac{1}{p^{\frac{n}{2}-1}} \left(\sqrt{\frac{1}{p}} \right)^m f\left(\frac{1}{p}\right),$$

and with the same choice for $h(x)$ and $f(p)$

$$\begin{aligned} \frac{1}{(\sqrt{p})^{\frac{2n}{2}+m-1}} e^{-\frac{\sigma}{\sqrt{p}}} = \frac{x^{\frac{n}{2}}}{2^m \sqrt{\pi}} \int_0^{\infty} \frac{e^{-\frac{\sigma^2}{4s}} J_n(2\sqrt{xs}) \text{He}_m\left(\frac{\sigma}{2\sqrt{s}}\right) ds}{(\sqrt{s})^{n+m+1}} \\ (m=0, 1, 2, 3 \dots; n=0, 1, 2, 3 \dots). \end{aligned} \quad (33)$$

Here the *sum* of m and n (or $2n$) and not the *difference* $m-n$ (as in the foregoing) plays a rôle. Therefore we cannot obtain here a relation which is independent of some index, but we must take special values of m and n to get some interesting results (which will be done afterwards).

First we will draw attention to the fact that, operating with (II.) and then with (I.), we arrived at (following from (33))

$$\frac{1}{p^2} e^{-\frac{\sigma}{\sqrt{p}}} = \frac{x^2}{\sqrt{\pi} 2^{r-2n+1}} \times \int_0^\infty \frac{e^{-\frac{\sigma^2}{4s}} J_n(2\sqrt{xs}) \text{He}_{r-2n+1}\left(\frac{\sigma}{2\sqrt{s}}\right)}{(\sqrt{s})^{r-n+2}} ds, \quad (34)$$

($r \geq 2n-1$), i. e., to an interpretation of the same image that we had already interpreted by means of (25).

These interpretations being, of course, identical, gives us, after some transformations, the relation

$$\int_0^\infty e^{-z^2 u^2} J_n\left(\frac{1}{2u}\right) \text{He}_{r-2n+1}(zu) u^{r-n-1} du = 2z \int_0^\infty e^{-z^2 u^2} u^2 J_r(2z\sqrt{u}) du \quad (35)$$

for $r-2n+1 \geq 0$; $r=0, 1, 2, \dots$; $n=0, 1, 2, \dots$

This relation originated from the fact that the image of (34) was also interpreted by means of (25).

But this can also be done by means of (31), when we choose there m and n , so that $m-n=-r$. In order not to confuse the indices n in (31) and (34) (being independent of one another), we take in (31) for m and n the following values :

$$m \rightarrow \nu - r,$$

$$n \rightarrow \nu,$$

where ν may be any integral number, making

$$\nu - r \geq 0.$$

(since m had to be $0, 1, 2, 3 \dots$).

We then obtain the interpretation

$$\frac{e^{-\frac{\sigma}{\sqrt{x}}}}{p^{\frac{r}{2}}} = \frac{2}{\sqrt{\pi}} \frac{1}{(2\sqrt{x})^{\nu-r+1}} \times \int_0^\infty e^{-\frac{s^2}{4x}} \text{He}_{\nu-r}\left(\frac{s}{2\sqrt{x}}\right) \left(\frac{s}{\sigma}\right)^{\frac{\nu}{2}} J_\nu(2\sqrt{s\sigma}) ds, \quad (36)$$

which for $\nu=r$ gives the interpretation (25), used above. Combining now (34) and (36) we arrive, after some transformations, at

$$\begin{aligned} \int_0^\infty e^{-z^2 u^2} J_n\left(\frac{1}{2u}\right) \text{He}_{r-2n+1}(zu) u^{r-n-1} du \\ = 2z \int_0^\infty e^{-z^2 u^2} \text{He}_{\nu-r}(zu) u^{\frac{\nu}{2}} J_\nu(2z\sqrt{u}) du, \end{aligned} \quad (37)$$

r, n, ν being positive integral numbers, including 0, and fulfilling

$$r \geq 2n-1, \quad \nu \geq r.$$

For $\nu=r$ we arrive, from (37), again at (35).

We now return to (33), where we will take some definite values for n and m .

For an application of the equation

$$F(\infty) = H(0), \quad . \quad . \quad . \quad . \quad . \quad (38)$$

it would be convenient in (33) to take

$$2n+m-1=0, \quad i. e., \quad n=0 \quad \text{and} \quad m=1.$$

$F(\infty)$ being then finite ($=1$), but this choice leads to an already known integral for Γ -functions.

For all other possible values of m and n we have

$$2n+m-1 > 0,$$

and, therefore,

$$F(\infty) = 0.$$

Now for $n > 0$ we have in the limit $x \rightarrow 0$,

$$x^2 J_n(2\sqrt{xs}) \rightarrow 0,$$

so that the relation (38) leads to the obvious result $0=0$.

But if we take

$$n=0,$$

we still get an interesting result

$$\int_0^{\infty} e^{-\frac{\sigma^2}{4s}} \text{He}_m \left(\frac{\sigma}{2\sqrt{s}} \right) s^{-\frac{m+1}{2}} ds = 0, \quad (m > 1),$$

which also may be written in the form

$$\int_0^{\infty} e^{-u^2} \text{He}_m(u) u^{m-2} du = 0, \quad (m > 1). \quad (39)$$

If we wish to apply the equation

$$\int_0^{\infty} \frac{F(p)}{p} dp = \int_0^{\infty} \frac{H(x)}{x} dx \quad . \quad . \quad . \quad (40)$$

to (33), or rather to (34), we first have to evaluate

$$\int_0^{\infty} x^{\frac{n}{2}-1} J_n(2\sqrt{xs}) ds = (n-1)! s^{-\frac{n}{2}*},$$

valid only for $n=1, 2, 3 \dots$

So we arrive at

$$\int_0^{\infty} e^{-\frac{\sigma^2}{4s}} \text{He}_{r-2n+1} \left(\frac{\sigma}{2\sqrt{s}} \right) s^{-\frac{r}{2}-1} ds = \frac{2^{r-2n+2} (r-1)! \sqrt{\pi}}{(n-1)! \sigma^r} \quad . \quad . \quad . \quad (41)$$

the right side being evaluated on the assumption $r=1, 2 \dots$ (excluding $r=0$).

After some transformation we obtain

$$\int_0^{\infty} e^{-u^2} \text{He}_{\rho-2\nu}(u) u^{\rho} du = \frac{\Pi(\rho) \Pi(\nu - \frac{1}{2})}{2 \Pi(2\nu)}, \quad . \quad . \quad (42)$$

valid for

$$\rho \geq 2\nu, \quad \rho = 0, 1, 2, 3, \dots; \quad \nu = 0, 1, 2, 3, \dots$$

All the above relations with Hermite polynomials followed from the combination of (II.) with (I.)

We could also have combined (II.) (containing the Hermite polynomials) and (III.).

* This may be done by means of

$$x^{\frac{n}{2}} J_n(2\sqrt{x}) = \frac{1}{p^n} e^{-\frac{1}{p}},$$

followed by an application of the same equation.

Using first (III.) and then (II.), or first (II.) and then (III.), we interpret respectively

$$(\sqrt{p})^m \frac{\sqrt{p}}{\sqrt{p+1}} f(\sqrt{p+1}) \text{ and } \frac{p}{\sqrt{p^2+1}} (p^2+1)^{\frac{m}{4}} f(\sqrt[4]{p^2+1}).$$

Choosing again

$$h(x) = \delta(x - \sigma), \quad f(p) = pe^{-p\sigma},$$

the first interpretation gives

$$(\sqrt{p})^{m+1} e^{-\sigma\sqrt{p+1}} = \frac{2}{\sqrt{\pi}} \frac{1}{(2\sqrt{x})^{m+1}} \left[e^{-\frac{\sigma^2}{4x}} \text{He}_m \left(\frac{\sigma}{2\sqrt{x}} \right) - \sigma \int_{\sigma}^{\infty} e^{-\frac{s^2}{4x}} \text{He}_m \left(\frac{s}{2\sqrt{x}} \right) \frac{J_1(\sqrt{s^2 - \sigma^2})}{\sqrt{s^2 - \sigma^2}} ds \right]. \quad (43)$$

Application of (38) leads to $0=0$.

For an application of (40) we need first

$$\int_0^{\infty} x^{-\frac{m}{2} - \frac{3}{2}} e^{-\frac{\sigma^2}{4x}} \text{He}_m \left(\frac{\sigma}{2\sqrt{x}} \right) dx = \left(\frac{2}{\sigma} \right)^{m+1} \Pi(m) \sqrt{\pi}$$

(by means of (41)), and so we get

$$\int_0^{\infty} \frac{J_1(\sigma u)}{(u^2+1)^{\frac{m+2}{2}}} du = \frac{1}{\sigma} - \frac{\sigma^m}{\Pi(m)} \int_0^{\infty} e^{-\sigma\sqrt{t^2+1}} t^m dt. \quad (44)$$

Many other relations of this kind can be found in a similar way, but the choice we made will have been sufficient to show the fertility of the method.

In general, also, such kind of transformations and manipulations which were successful for deriving mathematical relations from the formerly known symbolic representations, can also be applied with more or less success to the new representations.

For an eventual use in future we summarize some of the results in the following list, being based upon

$$f(p) \doteq h(x),$$

$$n=0, 1, 2, 3 \dots; m=0, 1, 2, 3 \dots; r=0, 1, 2, 3 \dots$$

*List of Results, obtained above.***1. Symbolic Relations.**

$$\frac{1}{p^{n-1}} f\left(\frac{1}{p}\right) \doteq \int_0^\infty \left(\frac{x}{s}\right)^{\frac{n}{2}} J_n(2\sqrt{xs}) h(s) ds. \quad \dots \quad (\text{I.})$$

$$(\sqrt{p})^m f(\sqrt{p}) \doteq \frac{2}{\sqrt{\pi}} \frac{1}{(2\sqrt{x})^{m+1}} \int_0^\infty h(s) e^{-\frac{s^2}{4x}} \text{He}_m\left(\frac{s}{2\sqrt{x}}\right) ds, \quad \dots \quad (\text{II.})$$

or by means of (II. a) or (II. b).

$$\left. \begin{aligned} \frac{p}{\sqrt{p^2+1}} f(\sqrt{p^2+1}) \\ \doteq h(x) - \int_0^x h(\xi) \frac{\xi}{\sqrt{x^2-\xi^2}} J_1(\sqrt{x^2-\xi^2}) d\xi \\ \doteq h(x) - \int_0^x h(\sqrt{x^2-s^2}) J_1(s) ds. \end{aligned} \right\} \quad (\text{III.})$$

$$\begin{aligned} \frac{1}{p^n} e^{-\frac{\sqrt{p^2+1}}{p} \sigma} \\ \doteq \left(\frac{x}{\sigma}\right)^{\frac{n}{2}} J_n(2\sqrt{xs}) - \sigma \int_\sigma^\infty \left(\frac{x}{s}\right)^{\frac{n}{2}} \frac{J_n(2\sqrt{xs}) J_1(\sqrt{s^2-\sigma^2})}{\sqrt{s^2-\sigma^2}} ds, \quad \dots \quad (21) \end{aligned}$$

$$\frac{1}{p^2} e^{-\frac{\sigma}{\sqrt{p}}} \doteq \frac{1}{\sigma^{n+1}} \frac{1}{\sqrt{\pi x}} \int_0^\infty e^{-\frac{t^2}{4\sigma^2 x}} t^{\frac{n}{2}} J_n(2\sqrt{xt}) dt, \quad (25)$$

or by means of (34) or (36).

$$\sqrt{p} e^{-\sqrt{p+1} \sigma} \doteq \frac{1}{\sqrt{\pi x}} e^{-\frac{\sigma^2}{4x}} - \frac{\sigma}{\sqrt{\pi x}} \int_\sigma^\infty \frac{e^{-\frac{s^2}{4x}} J_1(\sqrt{s^2-\sigma^2})}{\sqrt{s^2-\sigma^2}} ds. \quad \dots \quad (23)$$

$$\begin{aligned} (\sqrt{p})^{m+1} e^{-\sigma \sqrt{p+1}} \doteq \frac{2}{\sqrt{\pi}} \frac{1}{(2\sqrt{x})^{m+1}} \left[e^{-\frac{\sigma^2}{4x}} \text{He}_m\left(\frac{\sigma}{2\sqrt{x}}\right) \right. \\ \left. - \sigma \int_\sigma^\infty e^{-\frac{s^2}{4x}} \text{He}_m\left(\frac{s}{2\sqrt{x}}\right) \frac{J_1(\sqrt{s^2-\sigma^2})}{\sqrt{s^2-\sigma^2}} ds \right]. \quad (43) \end{aligned}$$

2. *Mathematical Relations.*

$$\int_0^{\infty} e^{-u^2} u^{\frac{n}{2}} J_n(2\sqrt{y}u) \text{He}_{n+r}(u) du \\ = y^{\frac{n}{2}} \int_0^{\infty} e^{-u^2} J_0(2\sqrt{y}u) \text{He}_r(u) du. \quad (32)$$

$$\int_0^{\infty} e^{-z^2 u^2} J_n\left(\frac{1}{2u}\right) \text{He}_{r-2n+1}(zu) u^{r-n-1} du \\ = 2z \int_0^{\infty} e^{-z^2 u^2} u^{\frac{r}{2}} J_r(2z\sqrt{u}) du, \quad (35) \\ (r \geq 2n-1).$$

$$\int_0^{\infty} e^{-z^2 u^2} J_n\left(\frac{1}{2u}\right) \text{He}_{r-2n+1}(zu) u^{r-n-1} du \\ = 2z \int_0^{\infty} e^{-z^2 u^2} \text{He}_{m-1}(zu) u^{\frac{m}{2}} J_m(2z\sqrt{u}) du, \quad (37) \\ \text{for } r \geq 2n-1, \quad m \geq r.$$

$$\int_0^{\infty} e^{-u^2} \text{He}_m(u) u^{m-2} du = 0, \quad (m > 1). \quad (39)$$

$$\int_0^{\infty} e^{-u^2} \text{He}_{m-2n}(u) u^m du = \frac{\Pi(m)\Pi(n-\frac{1}{2})}{2\Pi(2n)}, \quad (42) \\ (m \geq 2n).$$

$$\int_0^{\infty} \frac{J_1(\sigma u)}{(u^2+1)^{\frac{m+2}{2}}} du = \frac{1}{\sigma} - \frac{\sigma^m}{\Pi(m)} \int_0^{\infty} e^{-\sigma\sqrt{t^2+1}} t \, dt. \quad (44)$$

Eindhoven.
May 6th, 1935.

LXXVIII. *Vibration of an Elastic Column.*

By J. G. JAGGER, M.A.*

IF an elastic column is subjected to any distribution of axial forces, p per unit length, then by expressing p in the form of a Fourier Series the particle displacement U_x and stress f_x at any point x along the bar can be determined. The method also allows account to be taken of

* Communicated by the Author.

a damping force proportional to the velocity at any point.

By way of example, consider a column fixed at one end, the other end being free, subjected to a suddenly applied force

$$\frac{w}{2} (1 - \cos wt) \text{ per unit length.}$$

Then

$$\begin{aligned} p &= \frac{w}{2} (1 - \cos wt) \frac{4}{\pi} \left[\sin \frac{\pi x}{2l} + \frac{1}{3} \sin \frac{3\pi x}{2l} \dots \right] \\ &= \frac{w}{2} (1 - \cos wt) \frac{4}{\pi} \sum_{i=1,3,5} \frac{1}{i} \sin \frac{i\pi x}{2l}. \end{aligned}$$

If A = cross-sectional area of column, ρ = density, f = compression stress, and K = damping factor, the motion of any element distance x from fixed end is given by

$$p - A \frac{\partial f}{\partial x} - K \frac{\partial U}{\partial t} = A \rho \frac{\partial^2 U}{\partial t^2}$$

$$\text{and } f_x = -E \frac{\partial U}{\partial x} \quad \text{and} \quad a^2 = \frac{E}{\rho},$$

so that

$$\begin{aligned} a^2 \frac{\partial^2 U}{\partial x^2} + \frac{1}{A\rho} \frac{w}{2} (1 - \cos wt) \frac{4}{\pi} \sum_{i=1,3,5, \text{ etc.}} \frac{1}{i} \sin \frac{i\pi x}{2l} \\ - \frac{K}{A\rho} \frac{\partial U}{\partial t} = \frac{\partial^2 U}{\partial t^2}. \end{aligned}$$

For a solution take

$$U_x = \sum_{i=1,3,5, \text{ etc.}} q_i \sin \frac{i\pi x}{2l},$$

where $q_i = f(t)$ only, then the equation to determine q_i is

$$\ddot{q}_i + \frac{K}{A\rho} \dot{q}_i + \frac{i^2 \pi^2 a^2}{4l^2} q_i = \frac{1}{i} \frac{1}{A\rho} \frac{w}{2} \frac{4}{\pi} (1 - \cos wt);$$

putting

$$\frac{K}{A\rho} = \delta w, \quad w_i = iw_0, \quad \text{and} \quad w_0 = cw,$$

where $w_0 = \frac{\pi a}{2l}$ (the fundamental frequency of column),

$$S = \frac{E}{l} = \text{stiffness of column,} \quad W = \frac{wl}{A}.$$

This can be written

$$\ddot{q}_i + \delta w \dot{q}_i + i^2 c^2 w^2 q_i = w^2 c^2 \frac{1}{i} \frac{W}{2S} \frac{16}{\pi^3} (1 - \cos wt),$$

giving

$$q_i = q_{i_1} + q_{i_2},$$

where forced vibration

$$= q_{i_2} = \frac{W}{2S} \frac{16}{\pi^3} \frac{1}{i^3} \left[1 - i^2 c^2 \frac{(i^2 c^2 - 1) \cos wt + \delta \sin wt}{(i^2 c^2 - 1)^2 + \delta^2} \right]$$

and free vibration

$$= q_{i_1} = e^{-\frac{\delta}{2} \frac{w}{i} t} [A_i \cos nwt + B_i \sin nwt] \quad \text{for } i^2 c^2 > \frac{\delta^2}{4},$$

$$n = \sqrt{c^2 i^2 - \frac{\delta^2}{4}},$$

$$= (A_i + B_i t) e^{-\frac{\delta}{2} \frac{w}{i} t} \quad \text{for } i^2 c^2 = \frac{\delta^2}{4},$$

$$= A_i e^{-\lambda_1 w t} + B_i e^{-\lambda_2 w t} \quad \text{for } i^2 c^2 < \frac{\delta^2}{4},$$

$$\lambda_1 \text{ and } \lambda_2 = \frac{\delta}{2} \pm \sqrt{\frac{\delta^2}{4} - i^2 c^2},$$

and the motion at any point and time is given by

$$U_x = \sum_{i=1, 3, 5, \text{etc.}} (q_{i_1} + q_{i_2}) \sin \frac{i\pi x}{2l}$$

and stress

$$f_x = -E \frac{\partial U}{\partial x} = -\frac{\pi}{2} S \sum_{i=1, 3, 5} i (q_{i_1} + q_{i_2}) \cos \frac{i\pi x}{2l}.$$

The constants A_i and B_i in each term are chosen to make $q_i = 0$ and $\frac{\partial q_i}{\partial t} = 0$ when $t = 0$, the initial conditions in this example.

The solution also satisfies the conditions that $U = 0$ when $x = 0$ and $\frac{\partial U}{\partial x} = 0$, i. e., $f = 0$ at $x = l$ for all values of t , the initial series and solution having been suitably chosen to do this.

With no damping, i. e., $\delta=0$, this reduces to

$$U_x = \sum_{i=1, 3, 5, \text{etc.}} \left[(A \cos w_i t + B \sin w_i t) + \frac{W}{2S} \frac{16}{\pi^3} \frac{1}{i^3} \left(1 - \frac{w_i^2}{w^2 - w_i^2} \cos w t \right) \right] \sin \frac{i\pi x}{2l}.$$

Evaluating A and B,

$$U_x = \frac{W}{2S} \frac{16}{\pi^3} \sum_{i=1, 3, 5, \text{etc.}} \frac{1}{i^3} \left[(1 - \cos w_i t) + \frac{w_i^2}{w^2 - w_i^2} (\cos w t - \cos w_i t) \right] \sin \frac{i\pi x}{2l}$$

and

$$f_x = - \frac{W}{2} \frac{8}{\pi^2} \sum_{i=1, 3, 5, \text{etc.}} \frac{1}{i^2} \left[(1 - \cos w_i t) + \frac{w_i^2}{w^2 - w_i^2} (\cos w t - \cos w_i t) \right] \cos \frac{i\pi x}{2l}.$$

By suitably choosing the series the method can be used in examples with other types of loading and end conditions.

LXXIX. *Electromagnetic Field Theory.* By T. LEWIS,
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Introduction.

CLASSICAL electromagnetic theory is partly field theory and partly substance theory. The field equations, other than the equations of definition, can be derived from the *principle of least action*. The *action* is made up of two parts; the one is called the *field action* and the other the *substance action*. The equations of motion of electrons are also derivable from the *principle of least action*, but the *action* is not quite the same as the *action* from which the field equations are derived—certain simplifications are made which result in the well-known equations of motion of the relativity electron.

* Communicated by the Author.

An alternative method of obtaining the equations of motion is to use *Lorentz's Principle of Motion*, which states that the total force acting on an electron is zero. This leads to the concept of *electromagnetic mass* and to additional terms in the equations of motion which are interpreted as being due to the reaction of the electron's radiation. Electromagnetic mass defined in this way is not equal to the electrostatic energy divided by the square of the velocity of light as required by the *principle of relativity*. Another drawback to the Lorentz and similar electrons is that they radiate energy in any accelerated motion in contradiction to the observed stability of matter.

McLaren* has proposed a theory of electrons which appears to have some advantages over Lorentz's and other theories of the same nature. In this theory an electron is simply the boundary of the region to which Maxwell's equations apply. "Regions occupied by matter are thus reduced to absolute vacua, all energy and momentum being electromagnetic and in the æther, not in matter. At the boundaries of æther and matter certain conditions have to be satisfied; these will be shown to be identical with those obtained by considering the boundary of a perfect reflector.

"The electric charge is the integral of the normal component of the electric force over any closed surface forming an internal boundary. Instead of substance we have merely a constant of integration."

McLaren then deduces the equations of the field and the equations of motion of matter from the *principle of least action*. The *action* he uses is simply the *field action* used in the usual theory. He applied these principles to obtain a theory of the magneton.

In the following pages we have developed McLaren's ideas of field theory and obtained some very interesting results. We note here that it is not necessary to regard the inside of an electron as an absolute vacuum. There is no reason why æther should be excluded from this region provided \mathbf{E} and \mathbf{H} , which specify its state, are zero there. The vector potential need not be zero inside the electron; it can have the form $\left(\frac{1}{c} \frac{\partial \psi}{\partial t}, -\text{grad } \psi\right)$.

* McLaren, 'Scientific Papers,' p. 49, Camb. Univ. Press. (1925).

The problem of keeping the electron from exploding does not arise any more than that of keeping a vortex ring from exploding. This is an artificially created difficulty arising from the illogical procedure of attempting to subdivide an entity.

Substance enters into this theory as a secondary concept; but it need not be introduced at all as such, only it is convenient to use terms which have always been associated with the theory of electricity. Mass and force are other terms which are introduced more for the sake of convenience than because they represent primary concepts.

We note the following points from the theory :—

(1) There is no radial component of the Poynting vector in the immediate neighbourhood of the electron when observed from a coordinate system in which the electron is instantaneously at rest. This is a direct consequence of the properties attributed to the surface of the electron.

(2) It yields a formula for the rest mass of the electron which is in harmony with Einstein's principle of *identification of mass and energy*.

(3) It contains classical dynamics and the dynamics of the relativity electron in an electrostatic field as limiting cases.

(4) When an electron moves in the presence of another electron the advanced and retarded potentials of the latter appear to play similar rôles in building up the action. This is due to a kind of equivalence of action and reaction between the two electrons.

Of these results only (1) is a consequence of the model which we have adopted for the electron. (2), (3), and (4) also hold when the Lorentz model is used. This is shown in § 6. We also show that the Lorentz electron does not necessarily involve the idea of substance other than the æther. Density and current appear as differential coefficients of a function, satisfying the wave equation, which is first introduced as a Lagrangian multiplier. The only *action* used is the *field action*.

An important feature of the theory developed here is the equivalent treatment given to the electron's field and the so-called *external* field. Most writers omit to

consider the effect, if any, which the electron's field exerts on the source of the *external* field, namely, other electrons or protons. This criticism applies to Born's use of the *principle of least action* in his modified electromagnetic field theory *. Had he made consistent use of the principle by considering the effect of the electron's field on the source of the external field his final results would have been modified—a factor $\frac{1}{2}$ would enter into some terms and upset the agreement between mass and energy. Even a radiation field must have had points of concentration to begin with, and a constant field must have a permanent source. The chief advantage of Born's theory is that it admits a point electron with finite energy. Its chief disadvantage is the non-linearity of the field equations.

§ 1. *The Action of the Electromagnetic Field transformed into a Boundary Integral.*

In order to shorten the work we shall have occasion to use the notation suitable to a four-dimensional Euclidean space in some of the calculations; but all the results will be translated into the usual space-time notation.

The coordinates in the two notations will be

$$(x_0, x_1, x_2, x_3) \equiv (ict, x, y, z).$$

The properties of the electromagnetic field can be described with the aid of a four-vector, the electromagnetic potential, whose components are

$$(\phi_0, \phi_1, \phi_2, \phi_3) \equiv (i\phi, \mathbf{a}), \quad . \quad . \quad . \quad (1.1)$$

where ϕ is a scalar and \mathbf{a} an ordinary space vector.

The electric and magnetic intensities are defined by the formula

$$H_{\alpha\beta} = \frac{\partial\phi_\beta}{\partial x_\alpha} - \frac{\partial\phi_\alpha}{\partial x_\beta}, \quad \alpha, \beta = 0, 1, 2, 3, \quad . \quad . \quad (1.2)$$

where

$$i(H_{10}, H_{20}, H_{30}) = \mathbf{E}, \quad (H_{23}, H_{31}, H_{12}) = \mathbf{H}. \quad (1.3)$$

* M. Born, Proc. Roy. Soc. A, vol. cxliii. p. 410; vol. cxliv. p. 423.
J. Frenkel, Proc. Roy. Soc. A, vol. cxlvi. p. 930.

The Lagrangian function is

$$L = \frac{1}{16\pi} H_{\alpha\beta} H_{\alpha\beta} = \frac{1}{8\pi} (H^2 - E^2), \quad (1.4)$$

and the total action

$$A = -i \iiint L dx_0 dx_1 dx_2 dx_3, \quad (1.5)$$

where the integration extends over the whole field external to electrons. The $-i$ is introduced in order to make A real.

Four of Maxwell's equations are satisfied in virtue of the equations of definition (1.2). The remaining four are embodied in the statement

$$\delta A = 0, \quad (1.6)$$

where δA is the increment of A consequent upon giving small continuous, but otherwise arbitrary, increments to the ϕ_α in any finite portion of the field. These equations are

$$\frac{\partial H_{\alpha\beta}}{\partial x_\beta} = 0, \quad \alpha = 0, 1, 2, 3. \quad (1.7)$$

It is sometimes convenient to make the ϕ_α satisfy the equation

$$\frac{\partial \phi_\alpha}{\partial x_\alpha} = 0, \quad \alpha = 0, 1, 2, 3. \quad (1.8)$$

so that

$$\frac{\partial^2 \phi_\alpha}{\partial x_\beta \partial x_\beta} = 0, \quad \alpha = 0, 1, 2, 3. \quad (1.9)$$

But imposing the condition (1.8) does not completely determine the vector potential. If ψ be a function satisfying (1.9),

$$\phi_\alpha - \frac{\partial \psi}{\partial x_\alpha} \quad (\alpha = 0, 1, 2, 3)$$

describe the same field as ϕ_α , and also satisfy (1.8). Use will be made of this indeterminacy in order to simplify boundary conditions.

The object of these paragraphs is to show that the equation (1.6) contains also the equations of motion of electrons. But δA must now be interpreted as the

increment of action due to a small continuous displacement of a finite portion of the canal traced out in space-time by an electron. To prove this it is convenient first of all to transform the action into an integral taken over the "surfaces" of the canals traced out by electrons and the "surface" at infinity. By "surface" we shall always mean a three-dimensional subspace.

In virtue of (1.7) we can write

$$L = \frac{1}{8\pi} \frac{\partial \phi_\beta}{\partial x_\alpha} H_{\alpha\beta} = \frac{1}{8\pi} \frac{\partial}{\partial x_\alpha} (\phi_\alpha H_{\alpha\beta}).$$

Partial integration of (1.5) gives

$$A = - \frac{i}{8\pi} \iiint \lambda_\alpha \phi_\beta H_{\alpha\beta} d\Omega + \Sigma \frac{i}{8\pi} \iiint \lambda_\alpha \phi_\beta H_{\alpha\beta} d\omega, \quad (1.8)$$

where $d\Omega$ is an element of "surface," bounding the field externally, which will be made to recede to infinity in all directions, and $d\omega$ is an element of the "surface" of a canal traced out by an electron. The λ_α are components of a unit four-vector "normal" to the "surface" and Σ means summation over all electrons.

In order to evaluate the contribution of a single electron to the total action we shall make use of a device analogous to that of moving axes in ordinary dynamics. It is always possible to find a coordinate system such that a point P of the electron's surface (surface, without the inverted commas, is used in the ordinary sense) is passing through the state of rest at the instant concerned, when viewed by an observer at rest in this coordinate system. This coordinate system can be called the "proper" coordinate system for the point at that instant. The direction of its time-axis is fixed, in fact it is tangent to the world-line traced out by P.

It follows that in the "proper" coordinate system λ_0 is zero at P and $(\lambda_1, \lambda_2, \lambda_3)$ are the direction cosines of the electron's surface.

Again, we can write

$$d\omega = dS icdt,$$

where dS is an element of the electron's surface at P and $icdt$ an element of the world-line of P in the "proper" coordinate system.

The contribution of a single electron is now seen to be

$$-\frac{1}{8\pi} \iiint \{ \phi_0 (\lambda_1 H_{10} + \lambda_2 H_{20} + \lambda_3 H_{30}) + \phi_1 (\lambda_2 H_{21} + \lambda_3 H_{31}) + \dots \} dS c dt,$$

bearing in mind that the integrand is calculated in a different coordinate system for each point of the "surface."

Reverting to the usual notation, with the aid of (1.1) and (1.3) this expression can be written

$$A_e = -\frac{1}{8\pi} \iiint (\mathbf{v}, \phi \mathbf{E} + [\mathbf{a}, \mathbf{H}]) dS c dt, \quad (1.10)$$

where \mathbf{v} is a unit vector normal to dS .

As external boundary of the field we shall take a segment of a "cylinder" traced out in space-time by a large closed surface enclosing all the electrons and limited by the three-dimensional planes $t = -t_1$, $t = t_2$. Ultimately the surface will be made to recede to infinity in all directions, and both t_1 and t_2 will be made infinite.

It follows at once that the contribution of the cylinder to the total action is

$$A_1 = \frac{1}{8\pi} \iiint (\mathbf{v}, \phi \mathbf{E} + [\mathbf{a}, \mathbf{H}]) dS c dt. \quad (1.11)$$

But since the surface is at rest t refers to a fixed coordinate system and is the same for all points of the surface.

At points on the "planes" $t = -t_1$, $t = t_2$,

$$\lambda_0 = 1, \quad \lambda_1 = \lambda_2 = \lambda_3 = 0,$$

and it can be shown that their contribution to the total action is

$$A_2 = \left[\frac{1}{8\pi} \iiint (\mathbf{a}, \mathbf{E}) dV \right]_{t_1}^{t_2}, \quad (1.12)$$

where dV is an element of volume in the coordinate system in which A_1 is evaluated. The integration extends over all space external to electrons at the instants $-t_1$ and t_2 respectively.

In the next section it will be shown that A_1 and A_2 do not contribute to δA when the world canal of an electron is slightly displaced.

§ 2. *The Effective Contribution of the External Boundary to the Total Action.*

We are not interested in the absolute value of the action, but only in those contributions which undergo variation on account of the infinitesimal variation of a finite portion of the "canal" traced out in space-time by an electron. In order to see how A_1 and A_2 are affected by this variation of the world canal we will make the assumption that the region of space-time in which the electromagnetic field is varied is bounded by two light cones, with vertices on the world canal of the electron, one on either side of the portion which is displaced. This amounts to making use of the retarded potential solutions of the field equations. The effect of reflexion at the surface of other electrons can be taken into account by taking the vertices of the cones sufficiently removed from one another.

There are two cases to be considered :

$$(a) \ c(t_2 - t) < r, \quad (b) \ c(t_2 - t) > r,$$

where r refers to the distance between the electron at time t and a point on the large surface S enclosing the electrons, and $0 \leq t \leq \tau$, τ being the duration of the disturbance of the electron measured in the fixed coordinate system relative to which A_1 and A_2 are calculated.

If (a) is satisfied, the disturbance has not reached S at time t_2 , and it follows that A_1 is not affected.

If, on the other hand, (b) is satisfied, the disturbance has passed over the surface S , so that A_2 remains unaffected.

We will deal with (a) first. The integral concerned is

$$I_2 = \frac{1}{8\pi} \iiint (\mathbf{a}, \mathbf{E}) \, dV \quad \dots \quad (2.1)$$

evaluated at the instant t_2 .

On account of the equations of definition (1.2) and (1.3)

$$(\mathbf{a}, \mathbf{E}) = - \left(\mathbf{a}, \frac{1}{c} \frac{\partial \mathbf{a}}{\partial t} + \text{grad } \phi \right) = - \frac{1}{2c} \frac{\partial}{\partial t} (\phi^2 + \mathbf{a}^2) - \text{div } \phi \mathbf{a}$$

by (1.8).

Transforming I_2 by partial integration leads to

$$I_2 = - \frac{1}{16\pi} \iiint \left[\frac{1}{c} \frac{\partial}{\partial t} (\phi^2 + \mathbf{a}^2) \right]_{t_2} dV - \frac{1}{8\pi} \iint (\mathbf{v}, \phi \mathbf{a}) \, dS, \quad \dots \quad (2.2)$$

where the second integral is taken over the surface of electrons and over the enclosing surface at time t_2 .

But the disturbance will not have reached the enclosing surface at time t_2 , so that portion of the integral is not varied and may be disregarded. Again, by taking t_2 sufficiently large we can ensure that the conditions at the surfaces of the other electrons remain unvaried. We need therefore consider only the volume integral, which can be evaluated as follows.

Any disturbance emitted at the electron at the instant t will be effective at all points of a sphere of radius $c(t_2 - t)$ at the instant t_2 , the centre of the sphere being at the position of the electron at the instant t . A disturbance emitted at the instant $t + dt$ will be effective at all points of a sphere of radius $c(t_2 - t - dt)$ at the instant t_2 , the centre of this sphere being at the position of the electron at the instant $t + dt$. (For this purpose we regard the electron as concentrated at a point.) It follows that the whole disturbance emitted during the interval dt is effective within a shell bounded by these two spheres. It is easily seen that the thickness of the shell is $Kcdt$, where

$$K = 1 - (R_0, \beta) = \frac{\partial t_2}{\partial t}, \quad \dots \quad (2.3)$$

R_0 being a unit vector along the radius, and βc the electron's velocity.

The part of the volume integral in (2.2) which will be affected by the disturbance of the electron whose duration is τ may be written

$$- \frac{1}{16\pi} \int_{c(t_2 - \tau)}^{ct_2} dt \int \int K \frac{\partial}{\partial t_2} (\phi^2 + a^2) R^2 d\omega,$$

where $R = c(t_2 - t)$ and $d\omega$ is an element of solid angle.

But, by (2.3),

$$K \frac{\partial}{\partial t_2} = \frac{\partial}{\partial t},$$

and the variation of R with t may be neglected provided it is sufficiently large. With this assumption integration with respect to t can be performed. The result is

$$J = - \frac{1}{16\pi} \left[\int \int (\phi^2 + a^2) R^2 d\omega \right]_{c(t_2 - \tau)}^{ct_2}. \quad \dots \quad (2.4)$$

J is the only portion of A_2 which can be affected by a disturbance of the type considered. It is the difference of two surface integrals, the one taken over a sphere of radius ct_2 at time t_2 and the other over a sphere of radius $c(t_2 - \tau)$ at the same instant t_2 . But the whole disturbance is located between these two spheres, and it vanishes at the spheres themselves. It follows that A_2 is not affected by the infinitesimal displacement of a finite portion of the space-time track of an electron.

When the inequality (b) is satisfied A_2 is not affected. It can be shown that A_1 also remains unaffected.

$$A_1 = \frac{c}{8\pi} \int_{-t_1}^t dt \iint (\mathbf{v}, \mathbf{F}) dS,$$

where

$$\begin{aligned} \mathbf{F} &= \phi \mathbf{E} + [\mathbf{a}, \mathbf{H}] = -\phi \left(\text{grad } \phi + \frac{1}{c} \frac{\partial \mathbf{a}}{\partial t} \right) + [\mathbf{a}, \text{curl } \mathbf{a}] \\ &= -\frac{1}{c} \frac{\partial}{\partial t} (\phi \mathbf{a}) - \frac{1}{2} \text{grad } \phi^2 - \mathbf{a} \text{ div } \mathbf{a} + [\mathbf{a}, \text{curl } \mathbf{a}]. \end{aligned} \quad (2.5)$$

If we write

$$\mathbf{P} = -\mathbf{a} \text{ div } \mathbf{a} + [\mathbf{a}, \text{curl } \mathbf{a}],$$

the x -component may be written in the form

$$P_x = \frac{1}{2} \left(-\frac{\partial P_{xx}}{\partial x} + \frac{\partial P_{xy}}{\partial y} + \frac{\partial P_{xz}}{\partial z} \right),$$

where

$$P_{xx} = -\frac{1}{2} (a_x^2 - a_y^2 - a_z^2), \quad P_{yy} = -a_x a_y, \quad P_{xz} = -a_x a_z.$$

This tensor can be regarded as representing a system of stresses analogous to those formed from the field components \mathbf{E} and \mathbf{H} .

The first term on the right-hand side can be integrated with respect to the time and disregarded, for it will not contribute to the variation of A_1 . The only portion that can undergo variation is

$$I_1 = \frac{c}{8\pi} \int_{-t_1}^{t_2} dt \iint (\mathbf{v}, -\text{grad } p + \mathbf{P}) dS, \quad (2.6)$$

where $p (= \frac{1}{2} \phi^2)$ may be interpreted as a hydrostatic pressure.

Now every term in the integrand of the integral (2.6) is a differential coefficient with respect to a space coordinate of a homogeneous quadratic function of the

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potentials (ϕ , a). It is assumed that these potentials vanish as $\frac{1}{r}$, so that the differential coefficient of any quadratic function will certainly vanish as $\frac{1}{r^2}$. Terms of the order $\frac{1}{r^3}$ need not be considered, because they contribute nothing to I_1 when r becomes infinite. Any quadratic function of the potentials may be expanded in the form

$$Q = \frac{f}{r^2} + \text{higher powers of } \frac{1}{r},$$

where f is a function of zero dimensions in r , the distance between the electron at time t' and a fixed point of the enclosing surface S .

Neglecting $\frac{1}{r^3}$ etc.,

$$\frac{\partial Q}{\partial x} = \frac{1}{r^2} \frac{\partial f}{\partial x} = \frac{1}{r^2} \left\{ \frac{\partial f}{\partial t'} \frac{\partial t'}{\partial x} \right\}.$$

But

$$\frac{\partial t'}{\partial x} = -\frac{1}{Kc} \cdot \frac{\partial r}{\partial x}, \text{ with } K = 1 - (r_0, \beta) = \frac{\partial t}{\partial t'}.$$

To the same order of approximation,

$$\begin{aligned} \int_{-t_1}^{t_2} r^2 \frac{\partial Q}{\partial x} dt &= -\frac{1}{c} \int_{-t_1}^{t_2} \frac{1}{K} \cdot \frac{\partial f}{\partial t'} \cdot \frac{\partial r}{\partial x} dt \\ &= -\frac{1}{c} \int_{-t_1}^{t_2} \frac{d}{dt} \left(f \cdot \frac{\partial r}{\partial x} \right) dt \\ &= -\frac{1}{c} \left[f \frac{\partial r}{\partial x} \right]_{-t_1}^{t_2}. \end{aligned}$$

But at times t_2 and $-t_1$ the field at S is undisturbed; for, since $t_2 > t + r/c$, the disturbance will have passed out through S at time t_2 . The field is not disturbed at time t_1 because advanced potentials have been rejected. It therefore follows that A_1 is not affected by an infinitesimal displacement of a finite portion of the world track of an electron.

We must now find the contribution to δA which can be attributed to the electron itself and the contribution due to the presence of other electrons. An electron will be treated as a perfectly reflecting surface and not as the source of the field. The next section will be devoted to the definition and properties of a perfectly reflecting surface.

§ 3. *The Properties of a perfectly Reflecting Surface.*

If at every point of a surface at rest the vectors \mathbf{E} and \mathbf{H} are normal and tangential to it respectively, the surface is said to be a perfect reflector. The second condition does not appear to be necessary, and, in general, it is not assumed to be necessary. McLaren*, however, in his "Theory of Gravity" arrives at this condition as one which necessarily holds at the surface of separation of matter and æther.

When a surface is in motion it is always possible to find a coordinate system such that a given point P is instantaneously at rest with respect to it. If dS is an element of surface surrounding P and if \mathbf{E} and \mathbf{H} (measured in the proper coordinate system) are normal and tangential to dS respectively, the element dS is said to be perfectly reflecting. The whole surface is said to be a perfect reflector if it satisfies the condition that every element of it is perfectly reflecting in accordance with the above definition. In general it will not be possible to find a coordinate system such that the whole surface is at rest relative to it at one and the same instant.

The significance of the definition lies in the fact that the Poynting vector, $\frac{c}{4\pi} [\mathbf{E}, \mathbf{H}]$, is tangential to the element of surface dS in the "proper" coordinate system at that point, i. e., no electromagnetic energy crosses the surface.

Another property of a perfectly reflecting surface is expressed by the vanishing of the closed integral

$$\Phi = \oint \{ \phi c dt - (\mathbf{a}, d\mathbf{r}) \}, \quad . \quad . \quad . \quad . \quad (3.1)$$

when the path of integration is a closed curve lying

* S. B. McLaren, Phil. Mag. vol. xxvi. 2, p. 636 (1913).

entirely in the three-dimensional continuum traced out by the reflecting surface in space time.

In the other notation

$$\Phi = - \oint \phi_{\alpha} dx_{\alpha}.$$

It can be transformed into a two-dimensional integral in accordance with Stokes's theorem, the region of integration being any continuous simply connected two-dimensional continuum bounded by the closed curve.

If u and v are two parameters defining this continuum and $\left| \frac{xy}{uv} \right|$ is the Jacobian of (x, y) with respect to (u, v) , then

$$\Phi = -\frac{1}{2} \iint H_{\alpha\beta} \left| \frac{x_{\alpha} x_{\beta}}{u v} \right| du dv.$$

Reverting to the usual notation

$$\Phi = \iint \{ cE_x \left| \frac{t x}{u v} \right| + \dots - H_x \left| \frac{y z}{u v} \right| - \dots \} du dv,$$

or, in vector notation,

$$\Phi = c \iint \left(\mathbf{E}, \left| \frac{t \mathbf{r}}{u v} \right| \right) du dv - \iint \left(\mathbf{H}, [\mathbf{r}_u \mathbf{r}_v] \right) du dv, \quad (3.2)$$

where \mathbf{r}_u stands for $\frac{\partial \mathbf{r}}{\partial u}$, etc.

We will first of all prove that Φ vanishes for an infinitesimal circuit.

As we are dealing with invariants we are at liberty to choose our coordinate system. Let us choose one in which the element of surface in which the infinitesimal circuit lies is instantaneously at rest. In this system \mathbf{E} is normal to the surface element, and hence to both the vectors \mathbf{r}_u and \mathbf{r}_v which lie in the surface. It follows that the first integral on the right-hand side of (3.2) vanishes. Again, \mathbf{H} is tangential to the surface element and $[\mathbf{r}_u, \mathbf{r}_v]$ is normal to it. This causes the second integral to vanish.

The theorem can be proved for an arbitrary closed curve in the usual way by dividing it into infinitesimal circuits.

If P is any point on the three-dimensional continuum

traced out by the reflecting surface in space time, and O a fixed point on it,

$$f(P) = \int_0^P \{\phi c dt - (\mathbf{a}, d\mathbf{r})\}. \quad (3.3)$$

is a one-valued function of the position of the point P , provided it is understood that the path of integration lies entirely in this continuum.

This result, together with the indeterminacy of ϕ and \mathbf{a} , allows us to choose the potentials, so that \mathbf{a} is normal to the reflecting surface at every point relative to the "proper" coordinate system for that point.

We saw in § 1 that (ϕ, \mathbf{a}) and

$$\left(\phi + \frac{1}{c} \frac{\partial \psi}{\partial t}, \mathbf{a} - \text{grad } \psi\right)$$

are equivalent for the purpose of describing the electromagnetic field. If \mathbf{a} is not normal to the reflecting surface in the "proper" coordinate system we can always make $\mathbf{a} - \text{grad } \psi$ satisfy this condition by a proper choice of ψ .

Let ψ be a function which reduces to

$$\psi(P) = -f(P) + \psi_1(P) \quad (3.4)$$

on the reflecting surface, where ψ_1 is a function whose space gradient at P is normal to the surface in the "proper" coordinate system.

It is easily seen from (3.3) that the tangential component of $\text{grad } \psi$ is equal to minus the tangential component of the original \mathbf{a} . It follows that $\mathbf{a} - \text{grad } \psi$ is normal to the surface in the "proper" coordinate system.

If we require the relation

$$\frac{1}{c} \frac{\partial \phi}{\partial t} + \text{div } \mathbf{a} = 0$$

to be satisfied, ψ must be a solution of the wave equation.

G. A. Schott* has given a formula for a function satisfying the wave equation in terms of its values and the values of its derivatives at a moving surface. The

* "The Kirchhoff Formula extended to a Moving Surface," W. R. Morgan, Phil. Mag. vol. ix. (1930).

formula is a natural extension of Kirchhoff's formula for a fixed surface.

We notice that if $\psi_1(P)$ is zero or constant, $\phi + \frac{1}{c} \frac{\partial \psi}{\partial t}$ is zero at P in the "proper" coordinate system for P.

Again, by suitably prescribing the normal component of grad ψ in the "proper" coordinate system the normal component of a can be made to vanish. In other words, ψ can be found so as to make the four vector (ϕ, a) lie entirely in the three-dimensional continuum traced out in space time by the reflecting surface. McLaren uses this result in his theory of the magneton, but his potentials are magnetic or conjugate potentials suitable for describing a field due to magnetic matter.

Lastly, we will prove that the surface integral

$$e = \frac{1}{4\pi} \iint (\mathbf{E}, d\mathbf{S}) \quad . \quad . \quad . \quad . \quad (3.5)$$

is constant, the integral being taken over the instantaneous position of a closed reflecting surface and any arbitrary fixed coordinate system used.

Let S' be a closed surface, at rest relative to the coordinate system used, which entirely surrounds S during an interval $t_1 \rightarrow t_2$. On account of the vanishing of $\text{div } \mathbf{E}$ and the absence of any singularities between S and S' the surface integral taken over S is equal to the corresponding integral taken over S' at the same instant. Hence we have merely to prove that

$$\frac{\partial}{\partial t} \iint (\mathbf{E}, d\mathbf{S}') = 0.$$

Since S' is fixed the left-hand side of this equation is equal to

$$c \iint (\text{curl } \mathbf{H}, d\mathbf{S}') = c \oint (\mathbf{H}, d\mathbf{s})$$

by Stokes's theorem

The line integral vanishes when the surface is closed. We have thus proved that the surface integral of the normal component of the electric force is constant. When e is different from zero it will be called the charge associated with the surface. It must not be thought of as substance on the surface, characterized by density and motion, and each element of which retains its identity

throughout all time. The nearest analogue is the constant circulation round a closed curve in two-dimensional hydrodynamics. The analogy is not very good, because in the hydrodynamical problem it is the tangential component of a vector that is integrated round the closed curve, and not the normal component.

§ 4. *The Contribution of Electrons to the Total Action.*

We found in § 1 that the contribution of a single electron to the action could be written in the form

$$A_e = -\frac{c}{8\pi} \iiint (\mathbf{v}, \phi \mathbf{E} + [\mathbf{a}, \mathbf{H}]) dS dt, \quad (4.1)$$

where the integrand has to be evaluated in the "proper" coordinate system for each element $dS dt$ of the region of integration.

It has already been said that the function of the electron is to reflect the field and play the part of internal boundary. The vectors \mathbf{E} and \mathbf{H} are assumed to be zero inside the electron, but it is not necessary to assume that ϕ and \mathbf{a} are zero as well. They can have the forms $\frac{1}{c} \frac{\partial \psi}{\partial t}$ and $-\text{grad } \psi$ respectively. In terms of a fluid æther one can say that inside the electron the fluid moves irrotationally, whereas the electromagnetic field is a region where it has rotational motion as well. McLaren *, in his "Theory of Gravity," regards matter as an æther source or sink, and introduces four dimensions as well as an absolute time. (He appears to have been the first to introduce five dimensions as a basis for unified field theory.) But the æther moves irrotationally in regions occupied by matter and with rotation elsewhere. The hydrodynamical analogy cannot be pressed too closely, because one of the four dimensions is not on a par with the other three; the square root of -1 enters as a factor in the components of vectors along the axis corresponding to it.

We will now make the assumption that, at any instant, a coordinate system exists such that every element of the electron's surface is instantaneously at rest relative to it—i. e., there exists a "proper" coordinate system for the electron as a whole. This assumption implies

* Phil. Mag. vol. xxvi. p. 636 (1913).

invariability of shape in the "proper" coordinate system, and can be regarded as a definition of rigidity. It is introduced for simplicity, and might require modification at a later stage in order to account for certain properties of electrons.

The charge of the electron is e , defined as in (3.5). If e happens to be zero the reflecting surface will behave like an electric doublet when in the presence of other electrons for which e is not zero. (Compare an uncharged conductor in the presence of a point charge.)

It will be assumed that ϕ and \mathbf{a} have been determined so that \mathbf{a} is normal to the electron's surface in the proper coordinate system. If a particular mode of calculation does not give this result, a function ψ can be found, as explained in § 3, such that $\mathbf{a} - \text{grad } \psi$ satisfies the above condition. But ψ must satisfy yet another condition in order to be useful. It has been assumed that, when a finite portion of the space-time track of an electron is varied, the values of ϕ and \mathbf{a} on the undisplaced portions are not affected by this displacement. It follows that $\psi(P)$ must satisfy the same condition. If $f(P)$ is defined by (3.3), and \bar{f} is the average value of $f(P)$ taken over the electron's surface in the "proper" coordinate system, so that it is a function of the "proper" time of the electron only, then

$$\psi(P) = \bar{f} - f(P) \quad . \quad . \quad . \quad . \quad . \quad (4.2)$$

satisfies the above condition.

Again, when \mathbf{a} is normal to the surface ϕ is constant over the surface in the "proper" coordinate system. (It is possible to choose $\psi(P)$ so as to make ϕ zero at the electron's surface; but this would not help, for A_1 and A_2 have been disposed of on the assumption that the condition which led to choosing $\psi(P)$ in accordance with (4.2) is satisfied.)

The vector product $[\mathbf{a}, \mathbf{H}]$ is now tangential to the electron's surface and contributes nothing to A_e .

We can now write

$$A_e = -\frac{c}{8\pi} \int \phi \, dt \iint (\mathbf{E}, d\mathbf{S}) = -\frac{c}{2} e \int \phi \, dt \quad . \quad (4.3)$$

The last formula represents fairly accurately the contribution of a single electron to the total action. It is simple in form, but the accurate determination of $\phi(t)$ is far from being a simple problem. It will be shown

in the next section, however, that a first approximation leads to the classical form of the action.

§ 5. *The approximate Form of the Action
of two Electrons.*

It is clear that the electromagnetic field is conditioned by the distribution and motion of electrons, though electrons must not be considered as sources of the field. It is equally true that the motion of electrons is conditioned by the field. In classical electrodynamics it is usually assumed that a knowledge of the motion of electric charges is sufficient to determine the field. The same assumption will be made for the purpose of this approximation, so that if the motions are known the action can be calculated without ambiguity. The natural motion is that which gives a stationary value of the action.

Again, the linearity of the field equations allows us to regard the field as being the superposition of several fields, though, from a physical point of view, any partitioning of the field in this way is artificial and more or less arbitrary. When, however, the electrons are sufficiently removed from one another the partitioning appears to be less arbitrary and certainly leads to useful results. Born adopts this procedure in his new field theory with less justification, for his equations are not linear.

Let us write

$$\phi = \phi_0 + \phi' \dots \dots \dots (5.1)$$

By ϕ_0 we shall understand the potential at the electron's surface when it is at a very great distance from all other electrons—we can call it the electron's electrostatic potential. ϕ' is due partly to the presence of other electrons and partly to the motion and reflecting properties of the electron itself. We can think of it as the sum of three contributions: (1) the contribution of other electrons calculated as if the first electron were absent; (2) a term involving the acceleration of the electron which gives rise to the so-called reaction of radiation; (3) a term due to reflexion and which vanishes with the radius of the electron. ϕ' will be constant over the surface of the electron in the "proper" coordinate system. The sum of (1) and (3) will be equal to the value which the external potential would have at the electron's centre in the latter's absence, provided

the square of the electron's radius is neglected and assuming there are no waves of wave-length comparable with the electron's radius.

Nothing can be said about contribution (2) without investigation. The usual model of the electron gives no guide, for, when the electron is the source of the field, radiation takes place even in the "proper" coordinate system when there is acceleration. One cannot say this offhand about the present model, for in the "proper" coordinate system there is no radial component of the Poynting flux in the neighbourhood of the electron. The acceleration appears to set up a circulation of the electromagnetic energy about the electron, and it would seem that radial flow of energy is due to convection—that is, it depends upon the electron's velocity as well. But for the present we will neglect any reaction of radiation which might exist, so that ϕ' is simply the external potential at the electron's centre calculated as if the electron itself were non-existent.

In future we will write ϕ for ϕ' , and put

$$mc^2 = \frac{1}{2}e\phi_0. \quad (5.2)$$

With this notation (4.3) becomes

$$A_e = -c \int \{mc^2 + \frac{1}{2}e\phi\} dt. \quad (5.3)$$

m is called the rest mass of the electron and mc^2 its rest energy. $\frac{1}{2}e\phi_0$ is called the electrostatic energy of the electron, so that the definition (5.2) is in harmony with the principle of identification of mass and energy as required by Relativity Theory.

In an arbitrary fixed coordinate system

$$A_e = - \int \{mc^2 \sqrt{1 - \beta^2} + \frac{1}{2}e\phi - \frac{1}{2}e(\boldsymbol{\beta}, \mathbf{a})\} c dt, \quad (5.4)$$

where $c\boldsymbol{\beta}$ is the velocity of the electron in this system.

Except for the factor $\frac{1}{2}$ the integrand on the right-hand side of (5.4) is the usual Lagrangian for an electron in an external field. But this factor is necessary if, for small velocities, the Lagrangian is to reduce to the classical Lagrangian of ordinary dynamics.

Let us consider a field in which there are two electrons moving with small velocities. Neglecting retardation and magnetic effects, the action of the two electrons becomes

$$A = \int \left\{ \frac{1}{2}m_1v_1^2 + \frac{1}{2}m_2v_2^2 - \frac{1}{2}(e_1\phi_{21} + e_2\phi_{12}) \right\} c dt = \int (T - V) c dt, \quad (5.5)$$

where

$$V = \frac{1}{2}(e_1\phi_{21} + e_2\phi_{12}) = \frac{1}{2} \left(\frac{e_1e_2}{r} + \frac{e_2e_1}{r} \right) = \frac{e_1e_2}{r} \text{ approximately}$$

and T is the classical kinetic energy. Thus classical dynamics is a limiting case of the present field theory.

The result (5.5) is a justification of the identification (5.2). It is often stated that classical electrodynamics is inconsistent with this result*.

The more exact form of the action of an electromagnetic field containing two electrons is

$$A = - \int \{ m_1 c^2 \sqrt{1 - \beta_1^2} + m_2 c^2 \sqrt{1 - \beta_2^2} + \frac{1}{2}(e_1\phi_{21} + e_2\phi_{12}) - \frac{1}{2}e_1(\beta_1, \mathbf{a}_{21}) - \frac{1}{2}(\beta_2, \mathbf{a}_{12}) \} c dt, \quad (5.6)$$

where $(\phi_{21}, \mathbf{a}_{21})$ are the potentials of electron 2 at the centre of electron 1 and $(\phi_{12}, \mathbf{a}_{12})$ the potentials of electron 1 at the centre of electron 2.

This expression for the action is by no means complete, and it has been obtained by adopting a procedure which is contrary to the spirit of a pure field theory, namely, partitioning the field among the electrons and assuming that a knowledge of the motion of an electron enables us to calculate its own field. The equations of motion, which are contained in

$$\delta A = 0$$

establishes a relation between the motion of an electron and the field of other electrons, which is equivalent to establishing a relation between the two fields and determining their interaction. This method gives satisfactory results provided the electrons do not approach one another too closely.

The actual form of the Lagrangian in (5.6) is not the one which is generally used in order to derive the equations of motion of an electron, but, as we have seen, it reduces to the proper form for small velocities and accelerations. This is not the only justification for it. In § 7 it will be shown that when one electron remains more or less at rest the Lagrangian is identical with the accepted Lagrangian for an electron moving in a constant electrostatic field. An electron can remain more or less at rest in the presence of another electron provided its mass is sufficiently great or its radius sufficiently small.

* J. Frenkel, Proc. Roy. Soc. A, vol. cxlvi. p. 930 (1934).

The mass and the radius are connected by the relation

$$mc^2 = \frac{1}{2} e \phi_0 = \frac{1}{2} \frac{e^2}{a}.$$

The difference between a proton and an electron lies in the sign of e and the magnitude of the radius a . Classical field theory is unable to account for the particular values of e and a which actually occur.

The form (5.6) is not a consequence of the particular model which we have adopted for the electron. In the next section it will be shown that the Lorentz-Larmor theory of electrons leads to the same form for the Lagrangian in the first approximation.

§ 6. *The Action of a Field due to Lorentz Electrons.*

The idea of substance other than æther has not been introduced into our field theory. Matter is a region where the æther moves irrotationally and the field is a region of rotational motion. The Lorentz model of the electron does not require the introduction of a substance either.

As in § 1 we write for the total action

$$A = -\frac{i}{16\pi} \iiint H_{\alpha\beta} H_{\alpha\beta} dx_0 dx_1 dx_2 dx_3, \quad (6.1)$$

but this time the field is assumed to extend continuously into the electron, and the integral is taken throughout the whole of space.

We assume that the ϕ_α satisfy the equation of conservation

$$\frac{\partial \phi_\alpha}{\partial x_\alpha} = 0 \quad . \quad . \quad . \quad . \quad . \quad (6.2)$$

everywhere, so that the ϕ_α are not all independent.

If ψ is an arbitrary function of the coordinates

$$\delta \iiint \psi \frac{\partial \phi_\alpha}{\partial x_\alpha} dx_0 dx_1 dx_2 dx_3 = 0 \quad . \quad . \quad (6.3)$$

The field equations are a consequence of

$$\delta A = 0,$$

subject to (6.3). It is easily verified that they are

$$\frac{\partial H_{\alpha\beta}}{\partial x_\alpha} - 4\pi \frac{\partial \psi}{\partial x} = 0, \quad \beta = 0, 1, 2, 3, \quad . \quad . \quad (6.4)$$

or, in the usual notation,

$$\operatorname{div} \mathbf{E} - 4\pi \frac{\partial \psi}{c \partial t} = 0, \operatorname{rot} \mathbf{H} - \frac{1}{c} \frac{\partial \mathbf{E}}{\partial t} + 4\pi \operatorname{grad} \psi = 0. \quad (6.5)$$

Differentiating (6.4) with respect to x_β , and summing with respect to β , leads to the equation

$$\nabla^2 \psi - \frac{1}{c^2} \frac{\partial^2 \psi}{\partial t^2} = 0. \quad (6.6)$$

Thus ψ , which was introduced as a Lagrangian multiplier, satisfies the wave equation and is characteristic of matter. Comparing equations (6.5) with the Larmor-Lorentz equations leads to the identifications

$$\rho = \frac{1}{c} \frac{\partial \psi}{\partial t}, \mathbf{j} = -\operatorname{grad} \psi, \quad (6.7)$$

where ρ is called the density of electric charge and \mathbf{j} the current density. The equation of conservation is satisfied in virtue of (6.6).

The Lorentz model of the electron is obtained by assuming ψ to be zero or constant everywhere except within a small volume which is approximately spherical when at rest. The differential coefficients will have to satisfy appropriate boundary conditions as in hydrodynamics. For a single electron at rest

$$\psi = -c\rho t + \text{constant}$$

inside a small sphere, where ρ is a constant. If the electron is in uniform motion the Lorentz transformation gives

$$\psi = -\rho(ct - \beta x) / \sqrt{1 - \beta^2}.$$

The general motion leads to a more complicated form of ψ .

Transforming (6.1) by partial integration, as in § 1, and using (6.4), we get

$$\begin{aligned} A &= \frac{i}{2} \iiint \frac{\partial \psi}{\partial x_\alpha} \phi_\alpha dx_0 dx_1 dx_2 dx_3 \\ &= -\frac{c}{2} \iiint \left\{ \phi \frac{\partial \psi}{c \partial t} + (\mathbf{a}, \operatorname{grad} \psi) \right\} dx dy dz dt, \quad (6.8) \end{aligned}$$

where it has been assumed that certain conditions of continuity are satisfied at the electron's surface. It is sufficient that the normal component of

$$\phi \mathbf{E} + [\mathbf{a}, \mathbf{H}]$$

should be continuous in the "proper" coordinate system.

Making the identifications (6.7),

$$A = -\frac{c}{2} \iiint \{ \rho \phi - (\mathbf{j}, \mathbf{a}) \} dx dy dz dt, \quad (6.8')$$

the integral being extended over regions occupied by electrons.

This is the form of the action used by Born *; but Born disregards the contribution of the electron whose motion is being investigated, so that ϕ and \mathbf{a} refer to the external field. It follows that he cannot arrive at the concept of electromagnetic mass. In his case the inertial mass turns out to be a Lagrangian multiplier arising from the invariant relation

$$-c^2 dt^2 + (dr, dr) = ds^2,$$

where ds is the space-time interval.

We will assume the existence of a "proper" coordinate system for the electron as a whole, as in the previous case. This implies that \mathbf{j} is zero in this system.

Let us write

$$\phi = \phi_0 + \phi',$$

where ϕ_0 is the electrostatic potential of the electron considered and ϕ' is due to other electrons and the first electron's acceleration.

The rest mass is now defined by

$$mc^2 = \frac{1}{2} \iiint \rho \phi_0 dx dy dz, \quad (6.9)$$

again in accordance with the requirements of Relativity Theory.

Neglecting the effect of the acceleration

$$\iiint \rho \phi' dx dy dz = e\phi \quad (6.10)$$

where ϕ is the average value of ϕ' taken throughout the electron's volume and e is now defined by the integral

$$e = \iiint \rho dx dy dz.$$

The expression for the action now becomes

$$A = -\Sigma \int \{ mc^2 + \frac{1}{2} e \phi \} c dt,$$

or, in an arbitrary fixed coordinate system,

$$A = -\Sigma \int \{ mc^2 \sqrt{1 - \beta^2} + \frac{1}{2} e \phi - \frac{1}{2} e (\boldsymbol{\beta}, \mathbf{a}) \} c dt, \quad (6.11)$$

where Σ stands for summation over all the electrons in the field.

* M. Born, *Ann. der Phys.* Bd. xxviii. i. p. 571 (1909).

We have arrived at the same approximate form of the action function as in § 5, but one cannot expect agreement in higher approximations.

§ 7. *The Effective Action of Two Electrons.*

By effective action we mean that part of the total action which is varied on account of the infinitesimal displacement of a portion of the space-time path of one of the electrons. Hence, if the path of electron 1 is varied the term $m_2\sqrt{1-\beta_2^2}$ remains unchanged and may be disregarded.

We will assume that the distance between the electrons is always great in comparison with their radii, so that the point laws of Lienárd and Wiechert give a sufficiently good approximation for the potentials of the Lorentz electron. It does not follow that they give a good approximation for the potentials of the perfectly reflecting electron, so that the result obtained in this section is not applicable to it without some modifications.

The effective action of the field of two electrons can be written in the form

$$A^* = - \int \left\{ m_1 c^2 \sqrt{1-\beta_1^2} + \frac{1}{2} e_1 e_2 \left[K_{2r_{21}} \right]_{r_2} (1 - (\beta_1, [\beta_2]_{\tau_2})) \right\} dt_1 \\ - \int \frac{1}{2} e_2 e_1 \left[K_{1r_{12}} \right]_{\tau_1} (1 - (\beta_2, [\beta_1]_{\tau_1})) dt_2 \quad (7.1)$$

In this formula r_{21} is the distance between electron 2 at time τ_2 and electron 1 at time t_1 , r_{12} the distance between electron 1 at time τ_1 and electron 2 at time t_2 , where

$$c\tau_1 = ct_2 - r_{12}, \quad c\tau_2 = ct_1 - r_{21}, \quad \dots \quad (7.2)$$

$$\text{and} \quad K_1 = 1 - (r_{12}^0, \beta_1), \quad K_2 = 1 - (r_{21}^0, \beta_2), \quad \dots \quad (7.3)$$

where r_{12}^0 and r_{21}^0 are unit vectors along r_{12} and r_{21} respectively.

Now if the path of electron 1 is disturbed at the instant t_1 the effect will be apparent at the position of electron 2 at the instant $t_1 + r_{12}'/c$, where, in general, r_{12}' must not be confused with r_{12} or r_{21} ; but it is convenient to establish a one-one correspondence between t_1 and t_2 by means of the relation

$$t_2 = t_1 + r_{12}'/c, \quad \dots \quad (7.4)$$

that is, we identify τ_1 with t_1 and therefore r_{12}' with r_{12} .

Varying t_1 and t_2 in (7.4), we arrive at the symmetrical formula

$$\delta t_2 \{1 - (r_{12}^0, \beta_2)\} = \delta t_1 \{1 - (r_{12}^0, \beta_1)\}. \quad (7.5)$$

If we write

$$K_2' = 1 - (r_{12}^0, \beta_2), \quad (7.6)$$

the relation (7.5) becomes

$$K_2' \delta t_2 = K_1 \delta t_1, \quad (7.7)$$

and the contribution of electron 2 to A^* may be written

$$A' = - \int \frac{1}{2} e_1 e_2 \left[\frac{1}{K_2' r_{12}} \right]_{t_2} \{1 - ([\beta_2]_{t_2}, \beta_1)\} c dt_1. \quad (7.8)$$

Now if we had neglected the contribution of electron 1 due to its field at electron 2, and had admitted advanced as well as retarded potentials, the contribution of the advanced potentials of electron 2 at electron 1 would have been precisely A' .

We can therefore write the total effective action in the form

$$A^* = - \int \{ mc^2 \sqrt{1 - \beta^2} + \frac{1}{2} e(\phi_r + \phi_a) - \frac{1}{2} e(\beta, a_r + a_a) \} c dt, \quad (7.9)$$

where the suffix a refers to the advanced potentials of other electrons at the position of electron 1 and the suffix r to the retarded potentials.

If one of the electrons has a mass which is large in comparison with the mass of the other we can find a coordinate system in which it is more or less permanently at rest. In this case its retarded and advanced potentials coincide, and A^* reduces to the accepted form of the action for an electron in a constant electrostatic field.

Conclusion.

We have shown that a pure field theory based on *Maxwell's equations* and the *principle of least action* leads to a theory of the electron which is at least as satisfactory as theories based on the notion of electric substance and the notion of force, such as Lorentz's theory. In some respects it is even more satisfactory—*e.g.*, it leads to the correct formula for the rest mass. Whether the theory allows the existence of stable systems of electrons (+ protons) such as atoms is a matter for

investigation. There appears to be no reason why this should not be the case. G. A. Schott *, working on other lines, has found a very encouraging result which has a bearing upon this problem. He has proved that a rigidly electrified sphere is capable of periodic orbits without radiating energy. A rigidly electrified sphere is not quite equivalent to the perfectly reflecting electron, but Schott's work indicates the kind of result to be expected for the latter model. This problem is left for a future investigation.

LXXX. Resistance Thermometry below 10° K.

By J. D. BABBITT and K. MENDELSSOHN *.

THE measurement of temperature below 10° K. presents considerable difficulty owing to the fact that in this range very few substances are known which have a large temperature coefficient. The gas thermometer is, of course, the ultimate standard, but its advantages as an accurate instrument are overcome by experimental difficulties. Below 2° K., also, the gas thermometer becomes less reliable, as at this temperature helium begins to deviate strongly from the ideal state, and the knowledge of the equation of state is not sufficiently accurate for all corrections. The vapour pressure thermometer is extremely useful, but its use is limited to a range from the critical temperature of helium (5.2° K.) to about 1° K. It is, furthermore, inconvenient for calorimetric measurements, as the heat of evaporation introduces a large and somewhat uncertain correction.

The temperature coefficient of the resistance of most metals is practically zero in this range, and it is only when we consider the phenomenon of supraconductivity that we find resistances, which change appreciably with temperature. But the most striking feature about supraconductivity is that the resistance vanishes in a very small temperature interval, so small, in fact, that an ordinary superconductor is of no use as a thermometer.

* G. A. Schott, *Phil. Mag.* ser. 7, vol. xv. p. 752 (1933).

† Communicated by Prof. F. A. Lindemann, Ph.D., F.R.S.

The shape of the transition curve of a great many pure metals and alloys has been investigated. The transition curve of a single crystal of a pure metal has by far the steepest slope and is practically discontinuous ⁽¹⁾. Polycrystalline metals and alloys show a transition curve with a greater temperature interval, but there is no superconductor yet known that could be used as a thermometer.

It has been discovered in Leiden ⁽²⁾, however, that phosphor-bronze, while it is not a superconductor in the sense that its resistance completely disappears, yet it shows a drop around 7° K. in the resistance temperature curve which may be related to the phenomenon of superconductivity. Below this temperature the resistance decreases gradually, so that there is almost a linear relation between the resistance and the temperature. This curve is reproducible ⁽³⁾, and the wire investigated forms a sensitive and accurate resistance thermometer in the temperature range in question. As this is a valuable property, we decided to investigate the resistance of different specimens of phosphor-bronze with the object of discovering what constitution and what previous treatment of the phosphor-bronze was associated with the gradual slope of the transition curve, and, if possible, we wished to use this information to prepare a thermometer for the helium range based on this temperature dependency of resistance due to superconductivity.

Method.

All of the measurements were carried out in a small helium liquefier working by the expansion method ⁽⁴⁾. The liquid helium remains within the liquefier, and it surrounds a cylindrical gas-filled space in which the specimen whose resistance is to be measured is placed.

Two different methods of measuring the temperature have been employed in these experiments depending on the range required and the accuracy demanded. For all temperatures above the critical point of helium a type of gas thermometer was used as described by one of us ⁽⁵⁾.

Below the critical point of helium, it is possible to obtain the temperatures from the vapour pressure of the liquid helium. For this purpose a mercury manometer was attached to the outlet tube of the helium

container. As a control experiment to determine a possible time lag in these temperature measurements, we placed a secondary thermometer in the experimental chamber in one experiment. A change of temperature of 0.1° in the helium chamber was recorded within less than three seconds. The resistance of the specimens was mostly measured by a voltmeter-ammeter method. In most cases the current was kept very small (of the order of 1 milliampere) to minimize Joule heating, but in some cases it was necessary to increase the current in order to obtain a measureable deflexion on the millivoltmeter. The resistance of one or two specimens was read directly on a Wheatstone bridge.

Phosphor-Bronze Wires.

Over a dozen different specimens of Phosphor-Bronze from two different sources were investigated of which only one specimen proved to be suitable as a thermometer.

(Specimen I. 0 : 04 (Table I).)

TABLE I.

Temp. °K.	R (ohms).	R/R _{15° C.}
[15° C.]	24.0	1.000
90	21.35	.888
20.3	21.00	.874
9.4	21.20	.883
9.15	21.35	.888
9.0	21.35	.888
7.85	21.28	.886
6.1	21.35	.888
4.7	21.08	.878
4.2	20.80	.866
2.91	21.20	.883
2.1	21.08	.878

This wire was supplied by Hartmann and Braun. Diameter 0.04. It was wound spirally on a glass rod and potential and current leads soldered on to ends. The leads were made of 40 S.W.G. eureka wire.

The resistance of this specimen remains practically constant below the boiling-point of liquid air and presents no points of interest for our purpose. It is typical of the

Specimen II. 0.049 (fig. 1; Table II.).

Fig. 1.

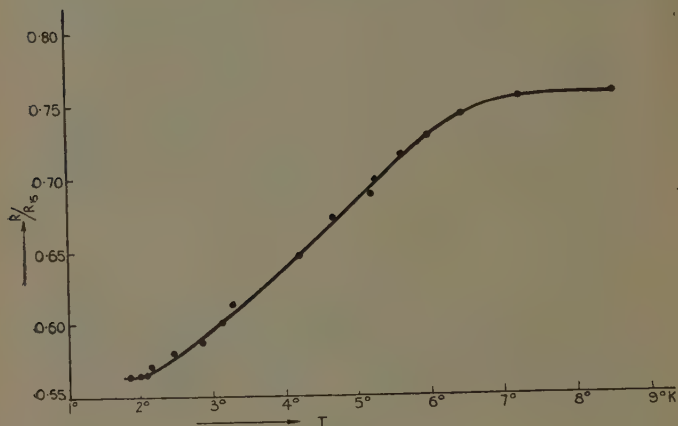


TABLE II.

Temp. $^{\circ}\text{K}$.	R (ohms).	R/R _{15$^{\circ}$ C.}
[15 $^{\circ}$ C.]	66.2	1.000
90	51.6	.779
20.3	49.6	.750
10.48	49.6	.750
8.52	49.9	.754
7.25	49.9	.754
6.45	49.2	.742
5.98	48.2	.728
5.61	47.4	.715
5.25	46.2	.698
5.2	45.4	.685
4.67	44.5	.672
4.2	42.8	.646
3.28	40.6	.614
3.12	39.75	.600
2.84	38.99	.589
2.47	38.40	.580
2.18	37.7	.570
2.06	37.42	.565
1.98	37.42	.565
1.93	37.35	.564

great majority of the phosphor-bronze wires investigated, and is the only one of this type for which the results will be given.

This wire was also supplied by Hartmann and Braun. It was mounted in a similar manner to the previous sample.

This is the wire which proved to be suitable for a thermometer. As the curve shows, the resistance begins to decrease about 7° K., and from there to the lowest temperature has a gradual slope. It is not quite linear, but has a slight inflection at the lower end. It agrees sub-

(Specimen II. 0.049, heat treated (Table III.).)

TABLE III.

Temp. °K.	R (ohms).	R/R _{15° C.}
[15° C.]	5.76	1.000
90	4.825	.838
20.3	4.75	.823
9.3	4.68	.813
9.2	4.68	.813
9.03	4.67	.812
8.8	4.645	.805
6.9	4.645	.805
4.95	4.645	.805
4.2	4.64	.805
2.1	4.64	.805

stantially with the curve obtained in Leiden for the phosphor-bronze thermometer ⁽²⁾.

Through the kindness of Dr. H. Moore a spectroscopic analysis was made from a small sample of the wire. By this means the following percentage composition was obtained:—Tin 7 per cent., phosphorus 0.2–0.25 per cent., and the following impurities were detected—bismuth, lead, silicon, calcium, and magnesium (the latter two possibly being due to surface contamination).

From another source ⁽⁶⁾ phosphor-bronze wire was obtained of almost identical composition. This was mounted in a similar manner to the first specimen. The results, however, showed its resistance to be independent of temperature from the boiling-point of hydrogen down

to the lowest temperature obtained (2° K.). This seems to lead to the conclusion that the method of manufacture of the wire has a large influence on the resistance temperature curve.

A sample of the wire II. which had already proved suitable for a thermometer was used. As it had already been shown that annealing destroyed the effect, it was decided to anneal and quench the wire, that is, to heat to a high temperature and then suddenly cool it. The sample of the wire was placed in a quartz tube and the tube evacuated and sealed. The whole was now heated in an electric furnace to about 900° C., which is just below the melting-point of phosphor-bronze. It was then suddenly cooled by dipping into water. That this treatment was effective in changing the structure of the wire was evident, as there was a very noticeable change in the physical properties of the wire. It was not nearly so springy as it had previously been.

It is evident from the results that the heat treatment has destroyed the temperature dependency of resistance.

(Specimen III. 0.04 (Table IV.).)

TABLE IV.

Temp. $^{\circ}$ K.	R (ohms).	R/R _{15$^{\circ}$ C.}
[15 $^{\circ}$ C.]	14.78	1.000
90	11.60	.785
20.3	10.60	.718
12.3	10.48	.708
10.05	10.48	.708
8.9	10.43	.706
8.2	10.40	.704
7.7	10.40	.704
7.2	10.38	.701
6.85	10.38	.701
6.50	10.38	.701
5.97	10.38	.701
5.70	10.12	.686
5.27	9.58	.649
5.1	9.04	.612
5.0	8.63	.584
4.75	7.51	.509
4.40	5.79	.392
4.20	5.01	.339
3.73	2.86	.193
3.65	2.618	.177

TABLE IV. (cont.).

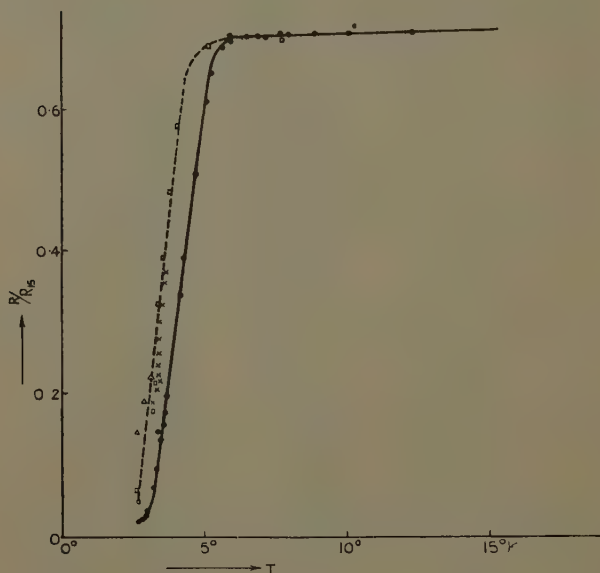
Temp. °K.	R (ohms).	R/R _{15° C.}
3.6	2.335	.1586
3.5	2.03	.137
3.41	1.548	.107
3.35	1.413	.0956
3.21	1.02	.069
3.01	0.572	.0387
2.94	0.413	.028
2.845	0.3645	.0247
2.78	0.3525	.0239
Field=256 Gauss.		
2.44	0.721	.0488
2.66	0.956	.0646
2.69	2.175	.147
3.11	3.29	.222
3.24	2.632	.178
2.93	2.818	.191
3.34	2.978	.215
3.41	3.782	.256
3.44	3.82	.258
3.65	5.80	.393
3.85	7.18	.486
4.10	8.51	.576
5.12	10.18	.689
5.95	10.18	.696
7.75	10.18	.696
Field=234 Gauss.		
3.32	2.761	.187
3.37	3.015	.204
3.40	3.190	.216
3.41	3.345	.2265
3.43	3.57	.2418
3.44	3.82	.2585
3.45	4.11	.278
3.46	4.49	.304
3.55	4.79	.324
3.65	5.23	.354
3.70	5.46	.370

Among the specimens of wire at our disposal the following proved to be of special interest. It was also one of the samples supplied by Hartmann and Braun and had a diameter of 0.04 mm. It was mounted on a glass rod in the usual way.

The resistance of this wire was also measured in a magnetic field at various temperatures. The field was obtained by a solenoid which fitted over the outside of the Dewar vessel. The field was perpendicular to the axis of the wire.

The resistance temperature curve for this wire is interesting for several reasons. In the first place it is in general similar in form to that obtained for II. The curve is practically horizontal until about 6° K. is reached, when it suddenly bends downwards. The initial transition temperature is about half a degree lower than for II. The greatest difference between the two wires, however, is to be seen in the slope of the curve. The resistance

Fig. 2.



of III. decreases to a tenth of its value in about 2.5°, whereas that of II. decreases to about four-fifths of its value in 3.5°. The former suggests a state approaching very close to that of a true superconductor. It is very similar to some of the curves shown by J. F. Allen ⁽⁷⁾ for alloys which are just on the border of the superconducting region.

That this decrease in resistance is due to superconductivity is further supported by the results obtained

when the resistance was measured in a magnetic field. Under these conditions we find that the transition does not take place until a lower temperature is reached and the whole transition curve is displaced. This phenomenon is characteristic of all superconductors. This wire also was "annealed and quenched." The results are given in Table V. and show that here, again, the decrease in resistance was destroyed by the heat treatment.

TABLE V.

Temp. °K.	R (ohms).	R/R _{15° C.}
[15° C.]	5.26	1.000
90	3.87	.735
20.3	3.52	.669
12.5	3.565	.678
4.2	3.455	.656
3.5	3.485	.662
1.95	3.26	.618

Discussion

Although the method of manufacture of the original wire is unknown to us in detail it must have been made by some process of drawing. This would leave all the individual crystals greatly elongated; they would be needle-shaped with their long axis parallel to the wire. If it may be assumed, as it is most likely, that the superconductivity is due to one distinct constituent of the alloy (either a pure metal or a solid solution), then it seems possible to offer a tentative explanation for the results obtained on phosphor-bronze. We know and have seen in one of our experiments that the transition to superconductivity can be displaced to lower temperatures by a magnetic field. The superconductive enclosures in the wire which, of course, are also needle-shaped, form chains through which the current passes. As soon as a needle becomes superconductive it forms a short circuit for the non-superconductive material of the wire, and the total resistance of the wire decreases. As the same current passes through all the needles which form a chain, the thinner needles will become superconductive

at lower temperatures than the thicker ones, and this would explain the gradual slope of the resistance-temperature curve.

A heat treatment of the wire relieves the strain and the needle-shaped crystal form disappears. This will result in our model in a breaking-up of the supraconductive chain, and no considerable decrease in resistance would be noticed. We want to emphasize, however, that this explanation has to be treated as a mere suggestion, which certainly cannot give a complete picture of the actual conditions.

Experiments ⁽⁸⁾ which have been carried out since this investigation was concluded have shown that the phenomena in supraconductive alloys are extremely complicated and that the inhomogeneity of concentration of a supraconductive in a non-supraconductive constituent may have a profound influence on the behaviour of the alloy.

Investigations of Binary Constituents.

As a further investigation into the properties of phosphor-bronze wires we attempted to find out if one of

Copper-Phosphorus Alloy (Table VI.).

TABLE VI.

Temp. °K.	R (ohms).	R/R _{15°C.}
[15° C.]	2.345	1.000
90	1.878	.799
20.3	1.755	.748
13.4	1.753	.746
11.3	1.753	.746
4.2	1.701	.725
2.66	1.689	.719
1.98	1.685	.718

the binary constituents of the wire could cause the drop in resistance. Phosphor-bronze has the following composition :—Copper 90–99 per cent.; tin 10–1 per cent; phosphorus 0.05–0.5 per cent. Of these three substances tin is the only one which shows supraconductivity. It

has a transition temperature of 3.7° K. As the curve for phosphor-bronze begins to decrease at about 7° K., it seems impossible that the effect is due to pure tin.

The binary alloy system Cu-Sn has been thoroughly investigated by J. F. Allen ⁽⁷⁾. It was found by him that when the concentration of copper became greater than 38 per cent. all signs of supraconductivity disappeared. Hence Cu-Sn cannot form the supraconductive component of phosphor-bronze which has 95 per cent. copper. This left the alloys tin-phosphorus and copper-phosphorus as possible sources of the supraconductivity. The copper-phosphorus temperature diagram is known ⁽⁹⁾. The temperature-concentration diagram of Sn-P has been investigated by A. C. Vivian ⁽¹⁰⁾. The low percentage phosphorus alloys contain a mixture of a solid solution and pure tin.

An alloy of copper-phosphorus was made by alloying 0.081 grams of phosphorus and 0.94 grams of copper. It is probable that this does not give the exact proportions in the alloy finally obtained, as the phosphorus is very volatile and some of it evaporated. The results show no sudden decrease in the resistance at low temperatures, and there is no sign of supraconductivity.

Tin-Phosphorus Alloy.

To prepare a specimen of this alloy, 2.63 grams of tin and 0.464 grams of phosphorus were melted together in a pyrex tube in a vacuum. Thus in the original mixture there was about 15 per cent. phosphorus. The final product, however, contained much less than this, as again it was impossible to prevent some of the phosphorus from evaporating. This specimen was again mounted on a glass tube and then annealed for 24 hours at a temperature of 216° . The results are given in Table VII. and plotted graphically in fig. 3.

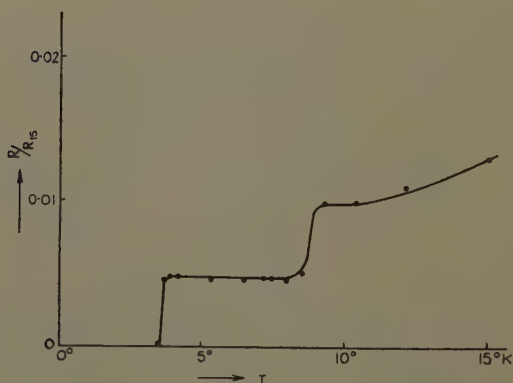
The curve shows two distinct supraconductive points for the same specimen. The temperature-concentration diagram for tin-phosphorus shows that the above specimen contains a eutectic mixture of tin and α -solution. It is evident that the lower break in the curve is due to the tin, as pure tin has a supraconducting point of 3.7° K. The obvious conclusion to draw is that the first transition must be caused by the α -solution of tin-phosphorus.

As the resistance does not completely disappear at this transition the α -solution cannot form a homogeneous

TABLE VII.

Temp. °K.	R (ohms).	R/R _{15° C.}
[15° C.]	7.10	1.000
15.0	.1502	.0212
12.1	.0928	.0131
10.4	.0781	.0110
9.3	.0708	.00998
8.5	.0698	.00983
7.9	.0354	.0050
7.4	.0334	.0047
7.15	.0333	.0047
6.5	.0333	.0047
5.35	.0333	.0047
3.95	.0335	.0047
3.70	.0332	.0047
3.23	.0000	.0000
3.55	Resistance increasing.	
3.70	.0308	.00435

Fig. 3.



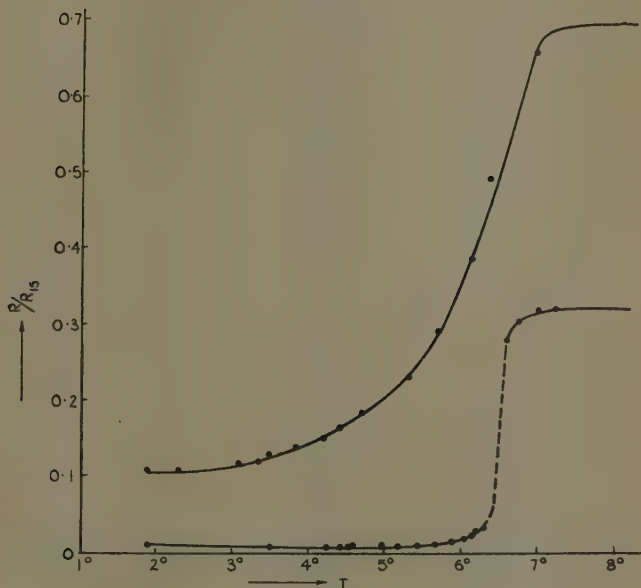
phase through the specimen, but instead the crystals of it must be so surrounded by tin that a resistance remains after all the α -solution has become supra-

conductive. A similar transition curve has been obtained by Meissner for titanium-nitride ⁽¹¹⁾.

It seems possible that this α -solution of tin-phosphorus is responsible for the temperature dependency of the phosphor-bronze, although we cannot exclude the possibility that a ternary alloy of copper-tin phosphorus or even an impurity (lead) may be responsible for the

Alloy of Lead-Silver. (Fig. 4, Tables VIII. and IX.)

Fig. 4.



phenomenon. The fact that the transition temperatures of phosphor-bronze and tin-phosphorus do not coincide can be explained by the observation of J. F. Allen ⁽⁷⁾ that, although the transition point of an alloy changes very little in eutectic regions, yet on the boundary of these regions, which is almost always a solid solution, it changes very rapidly with concentration.

As a final test of the conclusions arrived at in the investigations described above it was decided to attempt

TABLE VIII.

Temp. °K.	R (ohms).	R/R _{15° C.}
[15° C.]	2.243	1.000
11.9	.768	.342
4.45	.0247	.011
4.25	.0242	.0108
4.20	.0242	.0108
3.50	.0232	.01032
1.90	.0228	.01015
4.59	.0249	.0111
4.58	.0257	.0114
5.00	.0273	.0121
5.20	.0289	.0127
5.45	.0312	.0139
5.68	.0357	.0159
5.90	.0431	.0192
6.05	.0535	.0238
6.15	.0643	.0286
6.21	.0736	.0328
6.30	.0844	.0375
6.57	.639	.284
6.72	.707	.315
7.00	.733	.326
7.22	.735	.327

TABLE IX.

Temp. °K.	R (ohms).	R/R _{15° C.}
[15° C.]	1.769	1.000
90	1.419	.801
20.3	1.332	.753
12.3	1.291	.730
8.1	1.248	.704
6.95	1.179	.667
6.35	.881	.498
6.1	.691	.3905
5.69	.522	.2955
5.30	.419	.236
4.70	.333	.1882
4.4	.295	.167
4.2	.271	.153
3.85	.2497	.141
3.5	.229	.129
3.35	.212	.120
3.1	.1913	.108
2.3	.1913	.108
1.9	.1913	.108

to produce a wire having a temperature resistance curve approaching that of the phosphor-bronze. From a study of the curves given by Allen ⁽⁷⁾ it seemed as if a silver rich alloy of lead-silver would be most suitable. Allen finds that as the concentration of silver approaches the limiting value beyond which it is impossible to obtain supraconductivity the transition interval becomes greater. His investigation also led him to believe that there must be a solubility boundary at this region in the alloy system. It seems most likely in such a system that with a small increase of concentration of silver there would not be a sudden jump from a curve with a vertical transition to one completely horizontal. Although this change in concentration must be extremely small, yet it must be finite, and we therefore tried various lead-silver alloys in the range in question.

As it proved impossible to make the wires sufficiently thin by cold-drawing we rolled them. Although this will not give a crystal arrangement exactly similar to that obtained by drawing, yet by these means the crystals will be elongated, and we may expect a similar effect on the resistance.

Allen has found that the transition interval begins to increase with about 10 per cent. of lead. Hence it was decided to try alloys with 10, 8, 6, and 5 per cent. of lead. The alloys were cast in a capillary, then rolled as thin as possible, and a ribbon of suitable size was cut from them. For the specimens of 10 and 8 per cent. lead the transition curve was found to be practically vertical, and they proved uninteresting for our purpose.

The curves for the 6 and 5 per cent. alloys indicate that these two wires begin to show the desired effect. The 6 per cent. alloy deviates very little from the usual shape of the transition curve. The 5 per cent. alloy, however, shows a very appreciable temperature-range, and might be used as a thermometer between 7° K. and 3° K. By varying the concentration and the treatment still further it seems likely that a wire might be obtained possessing such a temperature-resistance curve as to make it suitable for use as a thermometer in the whole helium range.

Our thanks are due to Professor F. A. Lindemann, F.R.S., for many helpful suggestions and for his interest

in our work, to Miss J. R. Moore for help at the experiments, and to Imperial Chemical Industries, who, by their generosity, enabled one of us to carry out this research.

Summary.

The resistances of a number of phosphor-bronze wires were measured at low temperatures, only one of which proved suitable for a resistance thermometer. Investigations were carried out to determine what factors caused the temperature dependency of the resistance of this wire. It seems as if both the proportion of the constituents and the previous treatment accorded to the wire greatly affect the shape of the resistance curve.

A supraconductive component which may be responsible for the temperature dependency below 7° K. is tin-phosphorus, whose transition point was found to be 8.9° K. The results of the above investigations indicated that a binary alloy of a definite concentration and suitably treated would show a transition curve suitable for a thermometer. A wire of 5 per cent. lead in silver gave a resistance curve which shows that it can be used as a thermometer between 7° K. and 3° K.

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LXXXI. *X-ray and Magnetic Measurements of KCl Powders in Relation to Lattice Distortion and Photochemical Coloration.* By G. W. BRINDLEY, M.Sc., Ph.D., and F. W. SPIERS, Ph.D., University of Leeds, and F. E. HOARE, Ph.D., University College, Exeter*.

1. Introduction.

THE coloration of rocksalt, KCl, and other crystals when exposed to suitable radiations (ultra-violet light, X-rays, etc.), has been attributed by Smekal and others ⁽¹⁾ to the liberation of metallic atoms at cracks or flaws within the crystal, and this effect appears to be the greater the more imperfect the crystals.

In connexion with other experiments, we have been interested in the preparation of very finely divided crystals of KCl of the order of 10^{-4} – 10^{-5} cm. in size, and have attempted to obtain them by prolonged mechanical grinding, but the possibility that grinding might produce appreciable lattice distortion made powders obtained in this way of doubtful value for our work. The usual methods of precipitating KCl give crystals which are far too large, but by dissolving metallic potassium in alcohol and passing chlorine or HCl gas through the solution, a very fine precipitate is obtained. It was observed that when the precipitated powder and the finely ground powder were placed side by side in the path of an X-ray beam, the latter showed the coloration effect much more prominently. KCl powder was also prepared by rapidly cooling fused KCl and then grinding mechanically; this gave a photo-coloration of about the same magnitude as ordinary ground KCl. The difference in behaviour of the ground and precipitated powders is shown by the following observations:—Precipitated KCl when irradiated by $\text{CuK}\alpha$ radiation at about 5 cm. from the target of a Philips Metalix X-ray tube operated at 40 kilovolts and 20 milliamps., showed a faint violet coloration after an hour; the same coloration was obtained in five minutes or less with the ground KCl. When the two powders were exposed side by side for an hour or more, the ground powder showed a violet colour 5–10 times as strong as the precipitated powder.

* Communicated by Prof. R. Whiddington, F.R.S.

If the greater sensitivity of ground KCl is due to a greater number of internal flaws or to more extensive flaws, as Smekal suggests ⁽¹⁾, then it is of interest to consider whether the production of these flaws causes appreciable lattice distortion. A direct and quantitative method of measuring lattice distortion is to compare the intensities of X-ray reflexions from the distorted lattice with the intensities of the corresponding reflexions from the undistorted lattice; in the present case this involves comparing the intensities of reflexions from the two kinds of powders. Similar experiments have recently been carried out by two of us (G. W. B. and F. W. S.) to measure lattice distortion in filed metals ⁽²⁾.

One of us (F. E. H.) has been engaged on the accurate measurement of diamagnetic susceptibilities ⁽³⁾, and it seemed worth while to examine whether there was any measurable difference between the susceptibilities of KCl powders prepared in various ways. Since the diamagnetism of crystals depends very largely on the outer electrons of the ions, any large lattice imperfections may produce a measurable change in the diamagnetic susceptibility.

2. X-ray Measurements.

The method of investigation was the same as that previously described ⁽⁴⁾ for comparing X-ray reflexions from metal powders. A fine beam of X-rays was reflected from a plane stationary block of powder mounted at the centre of a cylindrical camera, and the reflexions were recorded on a photographic film wrapped round the outside. The powder holder contained two cavities filled with the two powders to be compared; either could be irradiated by raising or lowering the central rod on which the holder was mounted. For each setting of the powder holder with respect to the incident rays, a series of photographs was obtained by irradiating alternately one and then the other powder and raising the photographic film slightly after each exposure. The intensities of reflexion were measured with a Cambridge microphotometer.

It can be shown that the total intensity I_r reflected from a flat layer of powder of effectively infinite thickness is given by

$$I_r = (\text{constant}) p \cdot N^2 F^2 \phi(\theta) A / \mu, \quad . . . \quad (1)$$

where

p = multiplicity factor for the reflexion ;

N = number of unit cells per unit volume ;

F = amplitude reflected per unit cell in terms of the amplitude scattered by a single electron ;

$\phi(\theta) = [1 + \cos^2 2\theta] / [\sin \theta \sin 2\theta]$;

$A = [\sin (2\theta - \alpha)] / [\sin (2\theta - \alpha) + \sin \alpha]$;

α = angle between the powder surface and the incident X-ray beam ;

θ = glancing angle of reflexion ;

μ = coefficient of linear absorption of the X-rays in the material of the powders.

For KCl, $F = 4(f_K + f_{Cl})$ where f_K and f_{Cl} are the scattering factors of K and Cl respectively at room-temperature. When comparing reflexions from two specimens of KCl set at the same angle α , then p , N , $\phi(\theta)$, μ , and A will be the same for both powders, and any difference in the intensities will arise from a change in F due to lattice distortion *. It follows then that

$$\frac{I_r (\text{ppt. KCl})}{I_r (\text{ground KCl})} = \left[\frac{F (\text{ppt. KCl})}{F (\text{ground KCl})} \right]^2 \quad . \quad . \quad (2)$$

3. Measurements to detect Lattice Distortion.

To detect and measure lattice distortion, it is desirable for two reasons to consider reflexions of high order. In the first place, lattice distortion reduces the intensities of high order reflexions by a greater factor than the intensities of low order reflexions. Secondly, the effects of extinction have to be considered, and these are likely to be relatively unimportant for high order reflexions, but may be quite important for low order reflexions.

The highest order reflexion which can be obtained from KCl with $\text{CuK}\alpha$ radiation is the (800), which occurs at $2\theta = 157^\circ 36'$. Owing to the relatively small value of the multiplicity factor for this reflexion ($p=6$), it has a weak intensity, and is therefore not very suitable

* This assumes that both powders have a random orientation and that the results are not affected by extinction ; these questions are considered later.

for accurate measurement. The next highest order spectrum is the (642), which occurs at $2\theta=133^\circ 10'$; its multiplicity factor is 48, and it is therefore a comparatively strong reflexion. Measurements of this reflexion gave the following result:—

$$\frac{I_r(\text{ground KCl})}{I_r(\text{ppt. KCl})} = 0.98_5.$$

This result, together with similar results for other spectra which will be discussed later, indicates that KCl suffers very little lattice distortion when ground to a fine powder.

If the distortion is assumed to take, on the average, the form of a random displacement of the atoms from the points of the ideal lattice, then the magnitude of the mean displacement necessary to produce a reduction of intensity by a factor 0.98 can be calculated by using the following expression derived by Waller ⁽⁵⁾ for the reduction of intensity when the atoms of a cubic lattice are displaced randomly owing to heat motion:—

$$I/I_0 = e^{-2M}, \quad \text{where} \quad M = \frac{8\pi^2}{3} \left(\frac{\sin \theta}{\lambda} \right)^2 \cdot \bar{u}^2.$$

I_0 is the reflected intensity with the atoms at the lattice points; I is the intensity when the atoms are randomly displaced a distance $\sqrt{\bar{u}^2}$.

Taking $I/I_0=0.98$ for the (642) reflexion, we find $\sqrt{\bar{u}^2}=0.032 \text{ \AA.U.}$ This value may be compared with the distance between adjacent K and Cl atoms, 3.138 \AA.U. ; the average atomic displacement produced by grinding is therefore not greater than 1 per cent. of the interatomic distance.

These results are quite different from those obtained with metals and alloys. The process of filing metals, for example, broadens the X-ray reflexions and reduces their intensities considerably; in the case of copper, filing reduces the intensities of the (331) and (420) reflexions by approximately 30 per cent. It is evident that extensive grinding of an ionic crystal such as KCl does not produce distortions at all comparable with those produced in a metal by filing.

4. *The Question of Extinction.*

The interpretation of X-ray intensity measurements from large crystals and from powders is complicated

by the possibility that the results may be affected by extinction. Darwin ⁽⁶⁾ has distinguished between two kinds of extinction—primary and secondary. Primary extinction depends on the size of the individual crystal fragments, and if these are large the reflected intensity is reduced by the multiple reflexions within the fragments. Secondary extinction occurs if two fragments have exactly the same setting with respect to the incident X-ray beam and are so placed that reflexion from the first fragment reduces the intensity incident on the second. With powders secondary extinction is unlikely to be important unless there is a preferential orientation of the crystallites, but primary extinction will be important unless the individual crystals are exceedingly small (generally less than 10^{-4} cm. in size).

According to Darwin, primary extinction reduces the reflected intensity by a factor *

$$(\tanh xq)/xq \quad \text{where} \quad q = (Ne^2/mc^2)F \cdot d\lambda/\sin \theta.$$

In these expressions, x is the number of atomic planes taking part in the reflexion, q is the amplitude “reflected” by a single plane, d is the spacing of the planes, N , F , θ have already been defined, and e , m , and c have their usual significance. For purposes of calculation the following transformations are useful †:—Let L be an average linear dimension of a single crystal fragment. Then $x = L/d$. If a is the side of the unit cube of the lattice, then $N = 1/a^3$. Substituting for x and N , we obtain

$$xq = (e^2/mc^2)FL\lambda/a^3 \cdot \sin \theta. \quad . \quad . \quad . \quad (3)$$

In the case of KCl, $a = 6.276 \times 10^{-8}$ cm., $F = 4(f_K + f_{Cl})$, λ for $\text{CuK}\alpha$ radiation is 1.539×10^{-8} cm. Then we have

$$xq = \frac{(f_K + f_{Cl})\lambda}{\sin \theta} \times 4.558 \times 10^9 \cdot L, \quad . \quad . \quad . \quad (4)$$

whence $(\tanh xq)/xq$ can easily be calculated for particles of size L .

* This expression is usually written as $(\tanh mq)/mq$, but since m is being used in a different sense in the expression for q , it seems better to depart from the usual custom and write $(\tanh xq)/xq$.

† Darwin has pointed out that the extinction factor is best expressed in terms of the depth of the block, because this will be roughly the same in all directions, whereas the number of reflecting planes is not constant, but depends on the spacing of the planes considered.

5. *Primary Extinction in Precipitated KCl
and an Estimate of Crystal Size.*

In order to test whether primary extinction is appreciable for the powders used in this investigation, we have compared the observed results from the precipitated KCl powder with the intensities obtained by James and Brindley ⁽⁷⁾ using single crystals of KCl, which were corrected for extinction. These measurements were made with $\text{MoK}\alpha$ radiation, and a small correction is required to obtain the corresponding values for $\text{CuK}\alpha$ radiation. The details of this correction have been discussed in a paper by Brindley and Spiers ⁽⁸⁾, and need not be given here.

It follows from equation (1) that the *relative* intensities of reflexion from a plate of powder are given by

$$I_r = (\text{constant}) p(f_K + f_{Cl})^2 \cdot \phi(\theta) \cdot A \dots \dots (5)$$

In this equation $p(f_K + f_{Cl})^2 \phi(\theta)$ depends only on the reflexion considered; A depends on the setting of the plate with respect to the X-ray beam. The relative values of $p(f_K + f_{Cl})^2 \phi(\theta)$ obtained experimentally are compared with the calculated values in Table I. The first four columns of the table give the indices of the reflexions, the multiplicity factor p , and the scattering factors $(f_K + f_{Cl})$ at room-temperature interpolated from the values of James and Brindley ⁽⁷⁾ for $\text{MoK}\alpha$ radiation and the corrected values for $\text{CuK}\alpha$ radiation. The fifth and sixth columns give the calculated and experimental (relative) values of

$$p(f_K + f_{Cl})^2 \phi(\theta),$$

and the last column gives the ratio of the experimental to the calculated values.

Since the ratio of the experimental and calculated values is practically constant for all reflexions, there can be little primary or secondary extinction present in the precipitated KCl. We can safely say that for the (200) reflexion, for which extinction will have the *maximum* effect, the ratio of the observed to the calculated intensity is not less than 0.93 of the average value of this ratio for the remaining reflexions; this is equivalent to saying that if extinction exists at all in the precipitated KCl, it does not reduce the intensity of the (200) reflexion

by more than 7 per cent. Assuming that extinction of this magnitude is present and that it is wholly primary, we can calculate an *upper* limit for the average crystal size. Taking $(\tanh xq)/xq = 0.93$, we obtain from equation (4) $L = 5.3 \times 10^{-5}$ cm.

A direct microscopic determination of the crystal size is not possible, because the crystallites cling together in small clusters of the order of 5×10^{-4} cm. in size.

TABLE I.

Comparison of Observed and Calculated Intensities of X-ray Reflexions from KCl.

Spec- trum.	<i>p</i> .	$(f_K + f_{Cl}) \cdot$		$p(f_K + f_{Cl})^2 \cdot \phi(\theta).$		Ratio $\left(\frac{\text{Expt.}}{\text{Calc.}}\right).$
		MoK α .	CuK α .	Calc. (CuK α).	Expt. (relative values).	
200....	6	26.1	26.7 ₄	652×10^2	797 ..	1.22×10^{-2}
220....	12	20.8 ₅	21.4 ₅	386 ..	495	1.28 ..
222....	8	17.6 ₆	18.2 ₂	114 ₆ ..	152	1.33 ..
400....	6	15.4 ₂	15.9 ₈	46 ₃ ..	64	1.38 ..
420....	24	13.7 ₀	14.2 ₃	112 ₂ ..	151	1.35 ..
422....	24	12.2 ₀	12.7 ₁	72 ₆ ..	100.0	1.38 ..
442....	30	9.5 ₀	9.9 ₅	40 ₇ ..	52 ₇	1.30 ..
600....						
620....	24	8.7 ₈	9.2 ₁	27 ₉ ..	38 ₄	1.38 ..
622....	24	8.2 ₂	8.6 ₃	26 ₂ ..	32 ₂	1.23 ..
640....	24	7.3 ₆	7.7 ₁	25 ₉ ..	33 ₈	1.31 ..
642....	48	6.9 ₅	7.3 ₁	56 ₀ ..	68 ₄	1.22 ..
Mean value... 1.31×10^{-2}						

With crystals as small as 5×10^{-5} cm. primary extinction is negligible for all reflexions except the (200), and for this reflexion the intensity is reduced by 7 per cent.

6. Measurements with Mechanically Ground KCl considered in Relation to Primary Extinction, Crystal Size, and Orientation Effects.

The intensities of reflexion from ground KCl were compared directly with the corresponding reflexions

from the chemically precipitated powder. The results are given in Table II. The (200) and (400) reflexions from the ground powder are considerably enhanced; other low order spectra are reduced, and the high order spectra are approximately equal for the two powders.

As already remarked in section 3, the absence of any considerable decrease of intensity for the high order reflexions indicates that there is little or no lattice distortion produced by the grinding process.

The greatly increased intensities of the (200) and (400) reflexions are probably connected with the fact that the

TABLE II.

Comparison of X-ray Intensities from Mechanically Ground KCl and from Chemically Precipitated KCl.

Spectra.	$\left(\frac{I_r(\text{Ground KCl})}{I_r(\text{Pptd. KCl})} \right)$	No. of films measured.
200.....	1.62	17
220.....	0.86	10
222.....	0.85	6
400.....	1.64	5
420.....	0.97 ₅	4
442 + 600.....	0.96	3
620.....	0.97	3
642.....	0.98 ₅	3

(100) plane of KCl is the cleavage plane, and when the powder is ground the crystals probably break up as result of cleavage along this plane; then when the surface of the powder is smoothed over in the powder holder the (100) planes will tend to be aligned parallel to the surface. Although care was taken to avoid unduly compressing the powder, it seems inevitable that if the crystal fragments have been obtained by cleavage, the (100) planes will tend to be brought into alignment with the surface of the powder. Many photographs were taken of the (200) reflexion in order to see whether this alignment was at all exact. The setting of the powder holder was varied in steps of $0^{\circ}5$ over a range of 4° on either side of the glancing angle of reflexion, and essentially the same value was obtained

for the reflected intensity, which indicates that the crystal fragments are not exactly aligned by the smoothing process.

The decreased intensity of the (220) and (222) reflexions may arise in two ways. It may be due to primary extinction (in which case the average crystal size is of the order of 2×10^{-4} cm.), or it may be due to there being fewer (110) and (111) planes set to reflect radiation owing to the preferential setting of the (100) planes. Both factors probably contribute to the observed decrease of intensity, and the above estimate of the crystal size must therefore be taken as an approximate upper limit.

7. Conclusions from the X-ray Measurements.

From measurements of high order spectra it is shown that grinding produces very little, if any, lattice distortion in KCl, and that the mean atomic displacement is not greater than 1 per cent. of the interatomic distance of K and Cl.

Comparison of the relative X-ray intensities from precipitated KCl with calculated values (see Table I.), shows a reasonably constant ratio, which indicates (i.) that there is no preferential orientation of the powder particles; and (ii.) that there is little or no extinction. The intensity of the (200) reflexion is not reduced by more than 7 per cent. owing to extinction, and from this figure the crystal size is estimated to be of the order of 5×10^{-5} cm.

Comparisons of X-ray intensities from precipitated and ground KCl indicate (i.) that the high order spectra are approximately equal; (ii.) that the (200) and (400) reflexions from ground KCl are enhanced, probably due to preferential orientation of the powder particles; and (iii.) that other low order spectra from ground KCl are reduced possibly because of preferential orientation and primary extinction.

The investigation shows that the much greater photo-coloration of ground KCl is not an indication of considerable lattice distortion, and that the flaws or cracks to which the photo-coloration is attributed produce very little distortion of the lattice planes.

8. *Magnetic Measurements.*

As we have already mentioned in the introductory section, lattice distortion may affect the susceptibilities of crystals, since diamagnetism is largely dependent on the outer electrons of atoms, but without further knowledge of the form of lattice distortion it is difficult to predict whether an increase or decrease of susceptibility is to be expected. If the orbits of the outer electrons have, on the average, a greater mean square radius in undistorted than in distorted crystals, then distortion will reduce the numerical value of the susceptibility, and *vice versa*.

It is also very important in connexion with the accurate measurement of diamagnetic susceptibilities and their interpretation to know to what extent the experimental results depend on the mechanical treatment to which the crystals have been subjected.

Magnetic measurements have been made by a method previously described ⁽³⁾ on samples of KCl prepared by a variety of methods which have been grouped under headings (i.), (ii.), and (iii.) below.

(i.) *KCl finely powdered by Mechanical Grinding.*

In the course of previous work, measurements were made on KCl of A.R. purity * supplied by British Drug Houses, Ltd.; the salts were finely powdered and dried in a quartz crucible. The result obtained for the mass susceptibility † was 0.521×10^{-6} .

It was thought that the crystals might be further strained by powdering them after the KCl had been fused and rapidly cooled. The average result for powders prepared in this way was 0.520×10^{-6} , which is in very good agreement with the previous value and indicates that, if there is any effect due to the strained state of the crystals, there is not much difference in the state of strain produced by the salt being fused and rapidly cooled. A confirmation of this was afforded by the fact that the photo-coloration on exposure to X-rays was approximately the same for both these types of powder.

* A.R. = Analytical reagent.

† Throughout this section we give the numerical value of the diamagnetic susceptibility.

(ii.) *Finely precipitated KCl prepared from Metallic Potassium.*

This specimen was prepared by dissolving metallic potassium in absolute alcohol and precipitating with HCl gas; the specimen used was actually part of that prepared for the X-ray measurements. This specimen dried in lumps which with gentle pressure were easily crushed. For the magnetic measurements the KCl was introduced into the specimen tubes in the state in which it had dried. The susceptibility was found to be 0.526×10^{-6} , which is approximately 1 per cent. higher numerically than the result obtained with the ground specimens.

An attempt was now made to distort the precipitated KCl by grinding it in an agate mortar. The susceptibility, however, remained unchanged within the limits of experimental error, showing that no effect had been produced by the grinding. It seems very doubtful whether the process of grinding these very small crystals, of the order of 5×10^{-5} cm. in size, with an ordinary pestle and mortar can be very efficient, as the small irregularities on the grinding surfaces will probably be of the same order of magnitude as the crystal size, and thus only a fraction of the applied stress will be exerted on the crystals. This difficulty was also encountered in the X-ray investigation; it was only after very prolonged grinding that X-ray photographs showing no spots on the lines could be obtained (spots occur when the crystals are larger than 10^{-3} cm. approximately). It appears that ordinary grinding reduces the crystal size to 10^{-3} cm. without difficulty, and to 10^{-4} cm. if the grinding is continued long enough, but to obtain still smaller crystals other methods must be used⁽⁹⁾. It is therefore not surprising that an attempt to grind crystals of the order of 5×10^{-5} cm. in size led to a negative result.

(iii.) *Finely precipitated KCl prepared from KOH.*

Two methods of preparation were adopted starting with KOH of A.R. purity. The use of KOH had the advantage that it could be obtained of a high degree of purity much more easily than metallic potassium, and that it would be possible to find out whether the higher value of the susceptibility found for specimen (ii.) was due to impurities arising from the metallic potassium.

In the first case, KOH was dissolved in alcohol and KCl powder was precipitated with aqueous HCl of A.R. purity; in the second case HCl gas was used. Magnetic measurements upon the specimens prepared by both methods gave a result 0.527×10^{-6} , which is approximately the same as for specimen (ii.) and so confirms the slightly higher susceptibility for the precipitated KCl.

The results of the magnetic measurements are summarized in Table III.; the first column indicates the method of preparation, the second column gives the susceptibility and the average deviation from the mean, and the third column gives the corresponding susceptibilities per gram-molecule. The difference between

TABLE III.

Diamagnetic Susceptibilities of KCl Powders, $\chi \times 10^6$.

Method of preparation of specimen.	Susceptibilities, $\chi \times 10$.	
	per gram.	per gram-mol.
Ground KCl (A.R. purity)	$0.521 \pm 0.001_2$	38.8
Fused and ground KCl (A.R. purity) ..	$0.520 \pm 0.001_0$	38.7
Precipitated KCl, from metallic K . . .	$0.526 \pm 0.003_4$	39.2
Precipitated KCl, from KOH (A.R. } .. purity).	$0.527 \pm 0.002_8$	39.3

the susceptibilities of the ground and the precipitated powders is small, of the order of 1 per cent., but appears to be real.

X-ray examinations were made of all the specimens of precipitated KCl. The lines in the photographs of KCl prepared from metallic potassium were entirely free from spots, but the specimens prepared from KOH gave extremely spotty lines indicating the presence of relatively big crystals. It is suggested that the presence of water in the latter method might account for the precipitation of large crystals. The close agreement between the values for precipitated KCl prepared by the two methods suggests that, although the crystal growth has been rapid in the second method, no large strains are thereby set up. It is perhaps worth noting

in passing that all the specimens of precipitated KCl were slightly alkaline when tested by phenol phthalein.

In view of the smallness of the change in susceptibility due to grinding, it is important to consider the accuracy obtainable with the experimental arrangement. It has previously been estimated ⁽³⁾ that results accurate to $\frac{1}{2}$ per cent. could be obtained, but it was also observed ⁽¹⁰⁾ that somewhat larger errors might arise in experiments with very fine powders owing to the difficulty of packing such powders satisfactorily into the tubes used in the experiment. This difficulty was also found in the present work, and, in consequence, the results obtained from packing the powders into two tubes were not in such good agreement as is usually found; the average deviations shown in the second column of Table III. are greater for the precipitated salts than for the ground salts. In view of these considerations, we consider that the results given in Table III. are accurate to within 1 per cent. This is of the same order as the change in susceptibility due to grinding. It is the case, however, that all the results for precipitated KCl are higher than for ground KCl. Such a distinct tendency cannot be ignored, and the conclusion we draw is that there is a small alteration of the order of 1 per cent. in the susceptibility due to distortions, the effect being in a direction to decrease the numerical value of the susceptibility.

9. *Summary.*

Since a detailed summary of the X-ray measurements has already been given in section 7, it will only be necessary here to review the main results of the investigation.

The observation that mechanically ground KCl showed much greater photo-coloration than precipitated KCl when irradiated by X-rays, led us to investigate whether the internal cracks or flaws, to which this coloration is attributed, cause appreciable lattice distortion. Measurements of the intensities of X-ray reflexions of high order show that grinding produces very little lattice distortion; the average atomic displacement is not greater than 1 per cent. of the inter-atomic distance of K and Cl in the lattice. The question of extinction is considered in detail. Measurements of the diamagnetic susceptibilities of KCl produced in different ways show that

the effect of grinding is to reduce the susceptibility by about 1 per cent.; the gram-molecular susceptibility of precipitated KCl is 39.3×10^{-6} and of ground KCl, 38.8×10^{-6} .

These results show that the much greater photo-sensitivity of ground KCl is not an indication of large lattice distortion and that the internal cracks or flaws, on which the photo-sensitivity is thought to depend, do not give rise to any large distortions of the crystal planes throughout the volume of the crystals.

Acknowledgments.

The X-ray experiments here described have been carried out in the Physics Laboratories of the University of Leeds, and the magnetic measurements at University College, Exeter. We wish to express our thanks to Prof. Whiddington and to Prof. Newman for the facilities provided for carrying out this work, and to the Government Grant Committee of the Royal Society for a grant to two of us (G. W. B. and F. W. S.), with which some of the necessary apparatus was purchased.

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- (8) G. W. Brindley and F. W. Spiers, Phil. Mag. xx. p. 865 (1935).
- (9) Brentano, Phil. Mag. iv. p. 620 (1927), has also drawn attention to the difficulty of obtaining exceedingly small crystals by mechanical grinding; see p. 629 of this reference.
- (10) See ref. 3, p. 91.

LXXXII. *Variations in Colour Vision and Colour Measurement.* By T. SMITH, M.A., F.R.S. *

ABSTRACT.

WIDE variations in the coordinates of colours, which according to Houstoun and Younger are obtainable by individuals of normal colour vision and considered by them an objection to the use of the C.I.E. system, are shown to be due to errors of calculation or theory. The views of these authors on the unreliability of both direct and indirect colour measurements on the C.I.E. system are not in agreement with experience at the National Physical Laboratory.

IN their paper, "The Personal Error in Colorimetry" ⁽¹⁾, Dr. Houstoun and Mr. Younger discuss at some length variations in readings they have obtained in the measurement of certain colours, and related matters. Unfortunately some of the remarks they make are likely to create distrust of the C.I.E. system of colorimetry as a method of reaching definite measurements of colour. Workers with experience of the C.I.E. system, who realize its great potential value in industry as well as in science, will agree that these observations ought not to be passed by without comment. If any special justification is needed for openly traversing the views expressed in the paper it is provided by the fact that Dr. Houstoun is well known to be the author of a book and of several papers on colour questions; his remarks will therefore be widely regarded as those of an acknowledged authority on the subject. It is intended in this note to show that the paper contains a number of serious errors, and that the criticisms of the C.I.E. system are misconceived and cannot be maintained. The contention that some of their conclusions and methods are illegitimate will hardly come as a surprise to the authors.

An initial word of explanation is necessary. It is obvious enough that colorimetry in the ordinary sense is not possible with colour-blind observers. By "normal" colour vision we should now understand the vision of an

* Communicated by the Author.

individual who will not differ significantly in his colour matches from the C.I.E. standard observer. This, however, is not the sense in which Houstoun and Younger use the word. They appear to apply it to any one whose colour vision does not suffer from a major defect, *i. e.*, from some form of colour blindness. For instance, we are told that 123 of Coblentz and Emerson's subjects had normal colour vision, though these are divided into groups some of which are described as subnormal in some respect, while other groups are composed of unusually sensitive subjects. Again, the two authors are described as alike "normal," though it is obvious that they differ widely from one another in their colour matches. Thus "normal" in this paper seems to cover the range of vision for which trichromatic colorimetry is possible. The wisest course is perhaps to ignore this use of the word. So far as this note is concerned Younger would be classed as fairly normal but Houstoun as decidedly abnormal.

By some obscure line of reasoning, of which traces have appeared also in earlier publications, the fact that differences of colour vision manifest themselves as differences in direct measurements of colour appears to be regarded as a fault of or objection to the C.I.E. system of colorimetry. The C.I.E. system in fact contains, so far as we are concerned here, two essentials—an arbitrary but agreed system of numerical scales and a standard observer. The numerical reference system serves the same purpose as the arbitrary agreement to assign the numbers 0 and 100 as the temperatures on the Centigrade scale of matter in certain physically defined states. The outstanding difference is that, as there are three colour scales instead of one, four states (not more than four are permissible) have to be physically defined and assigned coordinates instead of two. The laws by which these scales have to be subdivided are well known in both problems, and the colour scales are therefore uniquely defined when the four points are chosen.

The definition of the standard observer would have been completely pointless had it not been known that variations in colour vision exist and that the definition provides an acceptable and efficient way of removing any uncertainty in colorimetric specifications attributable to this cause. This is the method of indirect colorimetry.

It is important to realize that the standard observer is defined solely for the exercise of this method. Any other uses require to be justified before they are adopted. Houstoun and Younger dismiss the indirect method cursorily by coupling it with a method depending on a tripartite "photoelectric observer," and adding the comment "the errors to which (these) two methods lie open are obvious and should not lead anyone wrong," the implication being that neither is to be trusted. Those who have the greatest experience of indirect colorimetry would disagree emphatically with this statement. It may at present be true of the photoelectric method, but it is not true of the C.I.E. method.

It may be noted that the authors raise no objection to the properties of the standard observer as a standard of "normal" colour vision; indeed, they make extensive use of him, but they have not considered whether or not their usage is logical and legitimate.

At the time the C.I.E. standards were described ⁽²⁾ it was only considered necessary to illustrate the application of the system to trichromatic colorimeters. This group probably still includes all general colorimetric apparatus in industrial use. The method of converting the readings of these instruments to the C.I.E. scales, while allowing for the observer's peculiarities of vision, is well known ⁽²⁾. The authors of the paper under discussion, however, use a vector colorimeter, which must be treated in a different way. Although they claim that "accurate" colorimetry can be done with this instrument, they have clearly not succeeded so far in expressing their results correctly on the C.I.E. system. With a vector instrument an observer who is known to be in satisfactory agreement with the Standard Observer may derive colour coordinates on the C.I.E. system by taking as applicable to his own vision the spectral locus of the standard observer. In all other cases the observer must determine his own spectral locus before he can convert his measurements to any standard system. In this respect the vector colorimeter is at a serious disadvantage compared with a trichromatic instrument. Although this step is an essential preliminary to the use of their instrument for systematic measurements the authors have failed to carry it out. The extremely discordant results they have represented in fig. 2 of their *Phil. Mag.* S. 7. Vol. 20. No. 136. *Suppl.* Nov. 1935. 3 Z

paper should have warned them that their procedure was seriously in error. Their method appears to have been to adopt for each observer the standard observer's results. In this way they have failed to secure the adjustment for the individual observer which is obtained directly with the trichromatic instrument. Though they have assumed far more fixed points than the four actually available, they have failed to satisfy one of the fundamental conditions of the C.I.E. system; they are therefore not justified in claiming that their results are expressed on the C.I.E. scales. But it is possible to go farther. Mixing indiscriminately the properties of the standard observer and those of a real observer when they differ considerably only leads to confusion and contradiction: the figures mean nothing in the absence of complete experimental details. They belong to no system whatever, for the properties which have been combined are inconsistent with one another. The procedure may be compared with the application of a scale ruled for a thermometer of uniform bore to an uncalibrated tube known only to be decidedly irregular. The deductions which can be made from the paper are thus that the results represented in fig. 2 are not results according to the C.I.E. system, and that the discrepancies tell us nothing about the accuracy that would be obtained by a routine in harmony with it. If we accept the results at their face value we shall infer, on the basis of experience with a number of observers at the National Physical Laboratory, that Younger would be an average observer in the sense that, of observers near enough to the standard observer to be suited for industrial colour measurements, there are likely to be as many observers whose uncorrected measurements are nearer the standard observer's as farther away, and that Houstoun would be classed as an abnormal observer not well suited (on economic grounds) for industrial work.

Two observations may perhaps be made here which follow from what has just been stated. If (as appears inevitable) it be granted that the colorimeter of the authors is not an instrument on which any observer can readily determine his own mixture curves, it is quite unsuitable for industrial use; and, until numerous cross-checks have been made for various colours on this instrument by a number of observers whose mixture

and visibility curves have been accurately determined, the claim for "accuracy" is devoid of meaning. All who are interested in the progress of colorimetry and of our knowledge of variations in human vision will hope that the authors will repair the fault in their present work by determining their own characteristic curves and utilizing them in their measurements with this instrument. An accurate comparison on the same instrument of the vision of two persons who differ as considerably from one another as the authors would be of much interest. It can hardly be too strongly urged that this is by far the most satisfactory, if indeed it be not the only possible, way of obtaining precise knowledge on the subject.

The latter part of the paper is mainly concerned with the discussion of purely hypothetical problems on the vision of subjects concerning whom only the visibility curve is known. From these curves it is impossible to infer anything about the colour vision of the subjects unless it happens (as will be the case with most of these groups) to emerge from calculation that these visibility curves are not consistent with normal colour vision in the narrow sense. There is indeed no evidence whatever forthcoming that those types of vision are possible which the authors have attempted to derive by the procedure described. Their work is thus nothing more than an academic exercise in arithmetic.

But even so their results are wrong. They claim that their procedure alters only the visibility, and that the colour properties are unaffected. An alteration in the visibility curve with no difference in colour properties, however, is not to be brought about in this way. It is secured by merely altering the relative luminosity factors of the three units. Everything else, including the colour triangle itself, is unaffected. Indeed it is obvious, since no difference in colour vision means agreement in all colour matches, that any possible change in the visibility function alone will result in no alteration at all in the coordinates of any colour. The whole of the calculated results, including those given in fig. 3 of the paper, have not therefore the meaning attributed to them by the authors.

However, it may be replied that, though evidence of their existence is entirely wanting, it is at least not

impossible that types of colour vision exist which are equivalent to the combination of a filter and the standard observer as described, and that from this point of view the results shown should not be without interest. This may be granted, but the results given must then be rejected on a different ground, viz., that the authors have not followed a correct theory in ascertaining how such observers would place the equi-energy spectrum. The results shown are entirely different from those which would be derived by the correct procedure. We cannot calibrate a thermometer by merely taking a Centigrade scale from another instrument and adjusting it so that the zero is correctly located. We must also see that the 100° mark is correct, *i. e.*, that the length of the scale unit is appropriate for the new instrument. The same principle has to be applied at the fourth fixed point of the colour scales, but this essential step has been omitted by the authors. When the correct procedure is applied to the figures given on p. 1112 for the two extreme groups (B.S. and Sub. B) not only is the range of displacements from the standard observer's position much less than that shown, but the directions of the displacements are quite different from those plotted. The errors shown are due to the adoption of a method of calculation which does not correspond to any rational observational routine. Fig. 3 is therefore of no value as an indication of variations liable to arise in direct colorimetry. Experience in this work is far from supporting an expectation of such large variations. The positions which should have been found are not recorded here, as it is purely an assumption that they have any real bearing on the problem under discussion. Thus instead of adding to our knowledge of the errors liable to arise in systematic colorimetry the paper only illustrates errors which arise from faulty technique and incorrect theory. However, it is pertinent to add that the regions chosen by the authors for their illustrations are likely to show errors as great as can be found anywhere. The various determinations of the spectral locus so far made lead us to expect the greatest disagreements in the blue-green region. In the magenta region it is well known that the colour is very sensitive to changes in the illumination, so that useful comparisons require strict adherence to the specification. In this connexion the

remark, made later, on accidental variations in the current through the lamp is not very reassuring. It may also be observed that with some methods of applying vector colorimetry in this region small errors in the spectral components may give rise to very large errors in the coordinates of the colour measured. The particulars given in the paper do not enable any judgment to be formed on this point. If the authors carried out corresponding measurements with a trichromatic colorimeter it is unlikely that considerable differences would be found in the coordinates.

As a final comment on the technical matters discussed in the paper it may be said that the argument put forward on p. 1115 regarding measurements with a trichromatic colorimeter is fallacious—like the earlier work, it involves the assumption that the standard observer's spectral locus may be utilized as though it were the experimentally determined locus of the real observer.

At the end of their paper Houstoun and Younger suggest that if a legal dispute occurred involving C.I.E. colour measurements the system might well be thoroughly discredited. It may therefore be desirable to add some remarks on the position as it appears to the writer.

The only circumstances in which there is any likelihood of a dispute on colour measurements occurring in a court of law arise when it has to be decided whether a material falls within the conditions of a specification. The question can be settled by direct or indirect colorimetry according to the special circumstances. The procedure will be exactly that now followed in regular tests. Ultimately reliance is placed on the standard C.I.E. indirect method. Any disagreement in the results obtained by this method could be resolved into questions on the accuracy of the spectrophotometry, the accuracy of the arithmetic, and the accuracy of the theory on which the calculations were based. These are matters of fact which can be definitely determined—there would be no question of leaving a decision to an inexperienced jury. With the direct method the procedure is to make comparisons with standards carefully calibrated by the indirect method. This is invariably part of the routine followed in testing such objects as coloured signal glasses at the present time for agreement with British Standard Specifications. The direct observations thus relate only

to small differences between sample and standard. As care is taken to select observers whose differences from the standard observer are not great, the direct method is quite safe with this routine. Considerable departures from the normal would be revealed by measurements different from the standard observer's. With the majority of observers chosen at random the discrepancies are small, and they can, moreover, be readily corrected. Though it is possible to correct an abnormal observer (normal in Houstoun's sense) this proceeding is not economically justified, as better observers for the purpose are readily obtained. Discrepancies in direct measurements could thus be traced to faulty routine, or unsatisfactory instruments, or an abnormal observer, or wrong calculations. The correct C.I.E. result would emerge without difficulty.

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LXXXIII. *On the World-Trajectories in Milne's Theory.*
By V. V. NARLIKAR, Benares Hindu University, India*.

§ 1. *Introduction.*

IN this paper some new properties of the world trajectories in Milne's theory are obtained, assuming that the trajectories are described by particles possessing mass. This assumption does not play an important part in Milne's work, where the kinematical aspect of the world-structure and the geometrical properties of the trajectories

* Communicated by Prof. E. A. Milne, F.R.S. [In communicating this interesting paper I do not wish to imply that I adhere to the details of Prof. Narlikar's dynamical interpretation of my kinematic work. My own dynamical interpretation, which was completed before Prof. Narlikar's paper was received, and which is now in course of preparation for publication, is substantially different from Prof. Narlikar's, as I make no use of *mass* either as an empirical construct or an undefined concept, but reach it purely deductively. As, however, there are certain resemblances between Prof. Narlikar's work and my own, it seems desirable to put on record that Prof. Narlikar's paper was received by me on July 24th, 1935, and communicated by the next post. By this date my co-workers and some of my critics had been put in possession of my main new results.—E. A. M.]

have been emphasized. The properties of motion have led in an unforced manner to the identification of the particles describing world trajectories with the cosmic rays and the cosmic dust clouds. It may therefore be of some interest to examine some of the physical properties of the trajectories.

The invariant ξ plays an important part in Milne's treatment of gravitation; its physical significance is given here. Four out of the six integrals of Milne's equations of gravitation state that the orbit is a plane one, and the remaining integrals are found to be giving the laws of march of m and s with ξ , m being the relative mass of the particle and s the separation. It is also shown how the curvature of a trajectory as observed from the origin depends upon the relative mass of the particle and its time-rate of change.

§ 2. *An Interpretation of ξ .*

The gravitational equations of motion are

$$\begin{aligned}\ddot{x} &= (x - ut) \frac{Y}{X} G(\xi), & \ddot{y} &= (y - vt) \frac{Y}{X} G(\xi), \\ \ddot{z} &= (z - wt) \frac{Y}{X} G(\xi), & . & (1)\end{aligned}$$

where

$$\xi = Z^2/XY, \quad u = \dot{x}, \quad v = \dot{y}, \quad w = \dot{z},$$

and X, Y, Z are given by

$$\begin{aligned}X &= t^2 - (x^2 + y^2 + z^2)/c^2, & Y &= 1 - (u^2 + v^2 + w^2)/c^2, \\ Z &= t - (ux + vy + wz)/c^2.\end{aligned}$$

The function $G(\xi)$ is assumed, in the first instance, to be quite arbitrary.

By the definition of ξ ,

$$\xi^{1/2} = Z/(XY)^{1/2} = \frac{1}{2} \dot{X}/(XY)^{1/2}. \quad (2)$$

If, at time t , m is the relative mass of a particle moving in the gravitational field and m_0 its invariant mass,

$$m_0/m = Y^{1/2}. \quad (3)$$

In the special theory of relativity the "separation" is defined by

$$s/c = X^{1/2}. \quad (4)$$

Hence

$$\xi^{1/2} = \frac{m\dot{s}}{m_0 c} \quad \dots \quad (5)$$

Let us call $m\dot{s}$ the relative momentum and $m_0 c$ the invariant momentum. The ratio of the two momenta is $\xi^{1/2}$. By the definition of ξ we know that

$$(\xi-1)XY = \frac{1}{c^2} \{ \Sigma(x-ut)^2 \} - \frac{1}{c^4} \{ \Sigma(uy-vx)^2 \}.$$

If

$$x-ut=\alpha, \quad y-vt=\beta, \quad z-wt=\gamma,$$

we have, after a little simplification,

$$(\xi-1)XY = \frac{1}{c^2} (\alpha^2 + \beta^2 + \gamma^2)Y + \frac{1}{c^4} \{ (u\alpha + v\beta + w\gamma)^2 \}. \quad (6)$$

Hence ξ must exceed unity throughout the motion. The initial conditions have been so chosen by Milne that α, β, γ all vanish at $t=0$ and $\xi=1$. The possibility of α, β, γ all vanishing does not arise for $t>0$ in virtue of the property possessed by $G(\xi)$ that it is strictly negative.

Thus the relative momentum of the particle is initially equal to the invariant momentum, but as the motion progresses the former always exceeds the latter.

It is important to know the behaviour of ξ as a function of time. Differentiating ξ with respect to time we obtain

$$d\xi/dt = -2Z(\xi-1)[1+G(\xi)]/X. \quad \dots \quad (7)$$

Since $\xi=1$ at $t=0$ and $\xi>1$ for $t>0$ we have $d\xi/dt=0$ when $G(\xi)+1=0$ for $t>0$. It has been suggested by Milne that $d\xi/dt$ cannot vanish once the motion is started, and that as $d\xi/dt$ must ever be positive for $1<\xi<\infty$, $G(\xi)+1$ must be negative throughout this part of the motion. The assumption that $d\xi/dt$ does not vanish amounts to this: the relative momentum must always increase during the motion till at last it becomes infinite. Unless this assumption is made the restriction on $G(\xi)$ cannot be placed, viz., that $G(\xi)+1<0$ for $\xi>1$. Since ξ becomes infinite when t is still finite, a motion of deceleration follows till at last t is infinite. Thus the relative momentum becomes infinite at a finite epoch and at a finite distance in the experience of the observer at the origin; and then it diminishes till at last it tends to its initial value $m_0 c$ as $t \rightarrow \infty$.

§ 3. *The Six Integrals of the Gravitational Equations.*

From the equations of motion (1) it follows that

$$\ddot{x}/(x-\dot{x}t)=\ddot{y}/(y-\dot{y}t)=\ddot{z}/(z-\dot{z}t),$$

so that

$$x-p\dot{y}=q, \quad \dot{z}-p'\dot{y}=q', \quad . \quad . \quad . \quad (8)$$

and

$$\dot{x}-p\dot{y}=qt, \quad z-p'y=q't, \quad . \quad . \quad . \quad (9)$$

where p, q, p', q' are arbitrary constants. These four integrals show that the motion takes place in a plane passing through the origin. Another integral may be easily obtained from (7), using the relation $\dot{X}=2Z$: this is the X-integral in Milne's theory.

In order to examine the significance of the X-integral consider first the operator md/dt used in defining the relation (5) between s and $\xi^{1/2}$:

$$m \frac{d}{dt} = m_0 c \xi^{1/2} \frac{d}{ds} = D. \quad . \quad . \quad . \quad (10)$$

It is evident that if the operator D defined as above, operates on an invariant the result is also an invariant. D may therefore be called an invariant operator. The differential equation (7) may now be written in the form

$$sD^2s + (1+G)[(Ds)^2 - m_0^2c^2] = 0. \quad . \quad . \quad . \quad (11)$$

Owing to the sign of $1+G$ not only s and Ds remain positive from $\xi=1$ to $\xi=\infty$, but also D^2s . In the limiting case where $1+G$ identically vanishes $D^2s=0$. This means that $m\dot{s}$, or the relative momentum, remains constant throughout the motion. This may be considered as the analogue of Newton's first law of motion, and for an arbitrary G the equation (11), which involves the time-rate of change of the relative momentum, may then be interpreted as the analogue of Newton's second law.

The sixth integral in Milne's theory is the A -integral. By the definition of A

$$A^2 = 1 - \frac{f^2 Y}{c^2}, \quad . \quad . \quad . \quad . \quad (12)$$

where

$$f^2 = (\alpha^2 + \beta^2 + \gamma^2)/(\xi-1)XY. \quad . \quad . \quad . \quad (13)$$

Hence by (6)

$$\begin{aligned} \Lambda^2 &= 1 - \frac{Y}{c^2} \cdot \frac{(\alpha^2 + \beta^2 + \gamma^2)}{\frac{Y}{c^2}(\alpha^2 + \beta^2 + \gamma^2) + \frac{1}{c^4}(u\alpha + v\beta + w\gamma)^2} \\ &= \frac{(u\alpha + v\beta + w\gamma)^2/c^4}{Y(\alpha^2 + \beta^2 + \gamma^2)/c^2 + (u\alpha + v\beta + w\gamma)^2/c^4} \\ &= \frac{(tY - Z)^2}{(\xi - 1)XY} \quad \dots \quad (14) \end{aligned}$$

From this form of Λ and from the equation

$$dY/dt = -2Y(tY - Z)G(\xi)/X \quad \dots \quad (15)$$

the Y -integral comes out immediately. Since f is constant,

$$\int \frac{dY}{Y \left(1 - f^2 \frac{Y}{c^2}\right)^{1/2}} = -2 \int \frac{d\Lambda}{(1 - \Lambda^2)} = \int \frac{G d\xi}{\xi^{1/2}(\xi - 1)^{1/2}(1 + G)} \quad (16)$$

As $Y = m_0^2/m^2$, the last integral gives

$$\int \frac{dm}{\sqrt{m^2 - f^2 m_0^2/c^2}} = -\frac{1}{2} \int \frac{G d\xi}{\xi^{1/2}(\xi - 1)^{1/2}(1 + G)} \quad \dots \quad (17)$$

The march of m with ξ is given by this integral.

§ 4. *The Curvature of a World-Trajectory.*

Regarding the relative mass of a particle and its time-rate of change as observables, we now obtain a formula for the curvature of a world-trajectory in terms of these observables. With the usual notation the curvature k is given by

$$k = \frac{[(\ddot{x}\dot{y} - \dot{y}\ddot{x})^2 + (\dot{y}\ddot{z} - \ddot{z}\dot{y})^2 + (\ddot{z}\dot{x} - \dot{x}\ddot{z})^2]^{1/2}}{(x^2 + y^2 + z^2)^{3/2}} \quad \dots \quad (18)$$

Using (8) and (9), we have

$$\mu k = \ddot{y} / [A_1 \dot{y}^2 + 2A_2 \dot{y} + A_3]^{3/2},$$

where

$$\mu = [q^2 + q'^2 + (pq' - p'q)^2]^{1/2} \quad \dots \quad (19)$$

and

$$A_1 = p^2 + p'^2 + 1, \quad A_2 = pq + p'q', \quad A_3 = q^2 + q'^2. \quad (20)$$

$$1 - m_0^2/m^2 = (A_1 \dot{y}^2 + 2A_2 \dot{y} + A_3)/c^2.$$

Therefore

$$\frac{m_0^2}{m^3} m = \ddot{y}(A_1 \dot{y} + A_2) = \dot{y} \sqrt{[A_2^2 - A_1 \{A_3 - c^2(1 - m_0^2/m^2)\}]}.$$

Thus

$$k = \frac{m_0^2}{\mu c^3} \cdot \frac{m \dot{m}}{(m^2 - m_0^2)^{3/2}} \cdot \frac{1}{\sqrt{[m^2(A_2^2 - A_1 A_3 + A_1 c^2) - A_1 c^2 m_0^2]}} \quad \dots (21)$$

The observed curvature of a trajectory is dependent upon the general gravitational field whose effect becomes manifest here through m and \dot{m} .

NOTE.—Reference may be made to 'Relativity, Gravitation, and World-Structure,' by E. A. Milne (1935); especially to pp. 141–156.

Summary.

An interpretation of ξ and $d\xi/dt$ is given. An interpretation is also given of the six integrals of Milne's gravitational equations, one of which is found to give the analogues of the first two laws of motion due to Newton. The observed curvature of a world-trajectory is also expressed in terms of other observables.

LXXXIV. Notices respecting New Books.

The Fundamentals of Chemical Thermodynamics.—Part I. *Elementary Theory and Electro-Chemistry.* By J. A. V. BUTLER. Second Edition. [Pp. xv+253.] (McMillan, 1935. Price 7s. 6d. net.)

THE success achieved by this book is largely due to the author's recognition of the difficulties which are experienced by students who are making a first acquaintance with the application of thermodynamical principles to chemical problems. The new edition contains some fifty pages of additional material in which the author gives consideration to gas-solid equilibria, pH determinations, potentiometric titrations, oxidation-reduction indicators, and electrolytic phenomena. These additions add materially to the scope and value of the book, and the inclusion of solutions to most of the numerical examples in the text represents a further attractive feature of the new edition.

H. M. D.

Relativity, Gravitation, and World-Structure. By E. A. MILNE.
(International Series of Monographs on Physics.) [Pp.
365.] (Oxford University Press, 1935. Price 25s.)

THE general scheme of Milne's theory of the expanding universe is to lay down an abstract rational definition of a set of moving particles, thence to develop the properties of the set, and, finally, by identifying the "particles" with spiral nebulae, particles producing cosmic rays, etc., to compare the theoretical structure with the observed universe. The definition of the set, called the cosmological principle, is as follows: observers attached to the "fundamental" particles of the system (which are in *uniform* relative motion) are to observe the *same* series of configurations in time of the whole set of particles. But two further independent axioms are implicitly incorporated into the theory, viz., a definition of distance by means of light-signals and the assumption that all fundamental particles have coincided simultaneously at some epoch of their history. It is never clear which of the predictions of the theory are traceable to these two somewhat arbitrary axioms and which are true consequences of the cosmological principle. At any rate, the system of the fundamental particles does reproduce the observed linear velocity-distance relation found in the system of the spiral nebulae. It disagrees with contemporary observation in giving non-uniform spatial distribution to the nebulae and a continuous luminous background to the sky.

Accelerated particles also occur in the system as a consequence of its definition. The accelerations so found are called "gravitational," although they possess none of the observed properties of gravitational accelerations—in particular, the "inverse square law" property for small distances. On the other hand, an accelerated particle will, in a finite time, acquire a velocity so high that it is capable, by collision with slower moving matter, of producing a cosmic ray. Moreover, accelerated particles form agglomerations round the fundamental particles. A serious difficulty, which is not satisfactorily overcome by Milne, is that an accelerated particle must acquire, and may retain, the velocity of light, thus apparently turning itself into a light-ray.

Although the book contains numerous attacks on general relativity, the reader will probably be puzzled as to where the difference between this theory and Milne's comes in. Recent work indicates that Milne uses a certain non-Riemannian geometry in terms of which he defines the properties of his set of particles. Metric and its associated tensors thus play a subsidiary part in the theory, in complete contrast to the case of general relativity.

Higher Mathematics for Engineers and Physicists. By I. S. and L. S. SOKOLNIKOFF. (McGraw-Hill Publishing Company, Ltd. Price 24s. net.)

THE authors have included under one cover a clear and attractively presented account of many of the mathematical topics which are indispensable to the study of physical sciences.

Since the work includes much that the University student of physics normally receives purely as mathematical instruction, and, in addition, some of the important mathematical topics usually met in an honours physics course, the student who is familiar with its contents will be well equipped for the study of one of the books described as introductions to theoretical physics, and, in fact, will find some portions already covered. The authors need, therefore, make no apology for including physicists as well as engineers in the title.

After a chapter on elliptic integrals, the solution of equations, determinants and matrices, and infinite series are dealt with in turn. Partial differentiation, Fourier series, multiple integrals, line integrals, and improper integrals each receive a chapter, followed by ordinary and differential equations, the former quite extensively treated. Vector analysis, probability, and empirical formulæ next appear, and, in conclusion, a chapter on conformal representation by another author has been added.

Each chapter includes problems, some of which provide extensions to the text, and the independence of the chapters should also make convenient for reference a work which will be found a very useful text-book.

Electrons (+ and -), Protons, Photons, Neutrons, and Cosmic Rays. By ROBERT ANDREWS MILLIKAN. [Pp. 492+98 figs.] (Printed by the University of Chicago Press and published by the Cambridge University Press. Price 15s.)

DR. R. A. MILLIKAN'S *flair* for crystal clear writing and unambiguous presentment is so well known that his new book is sure of a warm welcome in many circles.

The title of the book is far too cumbrous to be pleasing or even tolerable. Here, to be sure, is an opportunity for someone to invent the right, pithy, descriptive *multum in parvo* word.

The first ten chapters are not very different from Millikan's earlier book 'The Electron,' the last edition of which appeared in 1924. To this very substantial original section have been added six entirely new chapters dealing with waves and particles, the positron, the spinning electron, transmission, and, of course, the neutron and cosmic rays.

These new chapters are eminently readable, and are clearly

intended to give a general account of the topics—an object which is very definitely attained.

Lavishly illustrated, and well printed by the University of Chicago Press, this book is to be warmly recommended—in particular to University students.

Origins and Development of Applied Chemistry. By J. R. PARTINGTON. [Pp. vii+597.] (Longmans, Green and Co., 1935. Price 45s. net.)

THIS is not merely a history of applied chemistry; on the contrary, it is a work of unique character, which gives a complete survey of the origins and development of the chemical arts and crafts during the periods associated with the earliest civilizations. The results of the most recent archaeological research relating to these periods have been utilized by the author in the preparation of the matter for this remarkable book, which is at once authoritative, readable, and of interest to the chemist, the archaeologist, and the historian. It is astonishing to learn that the very extensive investigations which this work implies have been conducted by the author single-handed.

Whilst most histories of chemistry and its applications begin with the period of the Greeks and Romans, we are here presented with a systematic account of the sources, methods of production, and uses of materials in Egypt, Babylonia and Assyria, the Ægean regions, Syria, and Palestine from the earliest times down to the Bronze Age. For the most part the treatment in each of the periods associated with these civilizations is arranged so as to provide in the first instance information of a general kind, followed by sections dealing with the metals and with the non-metals respectively. It is not possible to indicate the varied sources which have been drawn upon to provide the information which Professor Partington places in concise form at the disposal of his readers, but the fact that there are seven thousand footnote references, representing a total of approximately twenty-five thousand single citations, gives some idea of the extraordinary detail and the immense scope of the work. The indexing is a feature which deserves very special commendation.

The survey undertaken by Professor Partington leads to the realization that the knowledge of the use of materials which most historical writers ascribe to the classical period is very largely, if not wholly, derived from cultural periods of much greater antiquity. As the author points out, the study of the development of mankind has no aspect more significant than that which is concerned with the use of materials and this book can be most warmly recommended, not only to

chemists and archæologists, but indeed to all who are interested in the early stages of the development of human activity.

H. M. D.

Atomic Physics. By MAX BORN. Translated by J. DOUGALL. [Pp. xii+352.] (Blackie and Son, 1935. Price 17s. 6d.)

WITH the increasing multiplicity and complexity of specialized researches, both theoretical and experimental, in modern physics, there is an increasing need for good text-books which survey the new knowledge and bring it into relation with the old, though the value of such text-books for the progress of science is seldom given due recognition. The specialist is not always happy in attempting a general survey; but in this book Born has been remarkably successful. It should, perhaps, be specifically mentioned that the author deals not only with the theory, but also with the experimental work. In the body of the book theoretical discussions are given of the simpler questions; on more difficult questions the nature of the arguments is indicated, and results are quoted. Proofs of all the formulæ used are, however, given in an appendix.

The chapters deal with Kinetic Theory, Elementary Particles (including the neutron and the positron), the Nuclear Atom (with sections on heavy hydrogen and artificial radioactivity), Wave-Corpuscles, Atomic Structure and Spectral Lines, Electron Spin and the Pauli Principle, Quantum Statistics and Molecular Structure. Perhaps the most pleasing feature of the book is the lucid manner in which some of the more recondite modern conceptions are introduced, so that the reader becomes convinced of their essential reasonableness. Difficulties are nowhere evaded, and a very clear impression is conveyed of the present state of the theory.

Some of the chapters cover well-trodden ground, but seldom without the introduction of novel and illuminating points of view. Special mention may be made of the very up-to-date sections on nuclear physics, which give an excellent survey of recent work, and of the chapter on quantum statistics. This is certainly one of the most lucid introductions to Einstein-Bose and Fermi-Dirac statistics available in English, though the account of the applications is disappointingly brief.

For many readers the thirty-one sections of the appendix will be of great value. These give succinct mathematical discussions of typical questions of classical physics and of the older and newer quantum theory. As examples, the classical and wave mechanical derivations of the Rutherford scattering formula are given, the matrix and wave mechanical treatment of the oscillator, and a precise treatment of the Heisenberg uncertainty principle.

There is a short bibliography. The absence of other

references is perhaps unfortunate, for to readers of this book selected references would have been of service. The historical course of development is indicated by the frequent introduction of dates, an admirable plan, if not so novel as the author seems to suggest.

The book is well produced and contains a number of good plates; and the translator is to be congratulated on his flowing and readable style. The book may be strongly recommended to all honours students of physics as well as to research workers requiring an authoritative general survey of atomic physics written with a full appreciation of the present outlook.

Bessel Functions for Engineers. By N. W. McLACHLAN, D.Sc., M.I.M.E. (Oxford: the Clarendon Press. Price 15s. net.)

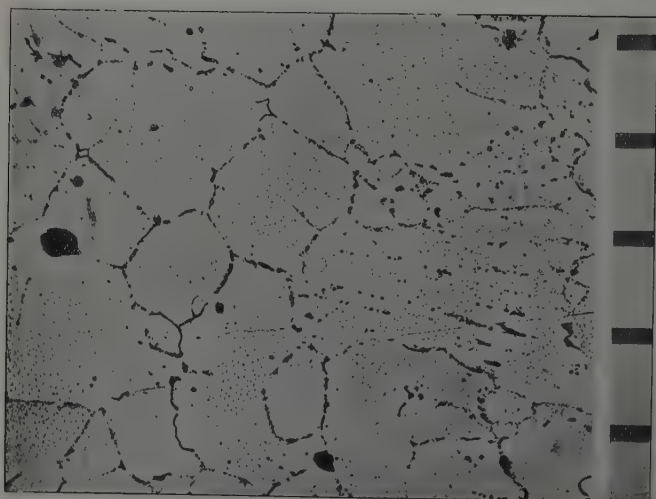
THE Theory of Bessel Functions has been extensively developed by Lommel, Graf and Gubler, Gray and Mathews, Schafheitlin and Watson: the application of these functions to problems in physics and engineering has received little attention beyond the references in Gray and Mathews. During the writing of his book, 'Loud Speakers,' Dr. McLachlan realized the necessity of a volume on Applied Bessel Functions. His 'Bessel Functions for Engineers' is the result, and is largely concerned with Radio and Electrical Engineering: problems in Structural Engineering and Elastic Stability, however, do not receive the same adequate treatment.

Of the functions related to those of Bessel, the Struve, Hypergeometric and Gamma functions, and Zonal Harmonics of integral order are referred to in some detail: the Ber and Bei functions, too, are fully treated, especially with reference to their application to the problems of alternating currents. The advantage of the polar form of Bessel Functions, derived from the asymptotic expansions and introduced some years ago by Prof. Kennelly, has been emphasized.

The author has added much to the value of his book by the inclusion of a large number of examples and exercises, with useful hints towards their solution, and a very complete list of formulæ and references to original papers: twelve pages of tables, to four significant figures are given; greater accuracy than this is occasionally required, and five or even six figures would have been welcomed; the zeros of Bessel Functions of small and large order do not appear among the tables. Although a few minor omissions have been noted in Dr. McLachlan's book, the author has, nevertheless, made an able and practical contribution to the subject and provided physicists and engineers with the equipment for solving many problems involving the use of these functions.

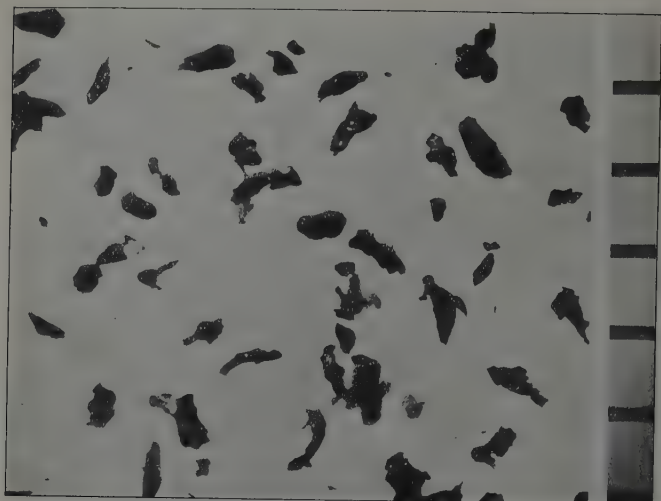
[The Editors do not hold themselves responsible for the views expressed by their correspondents.]

FIG. 1.



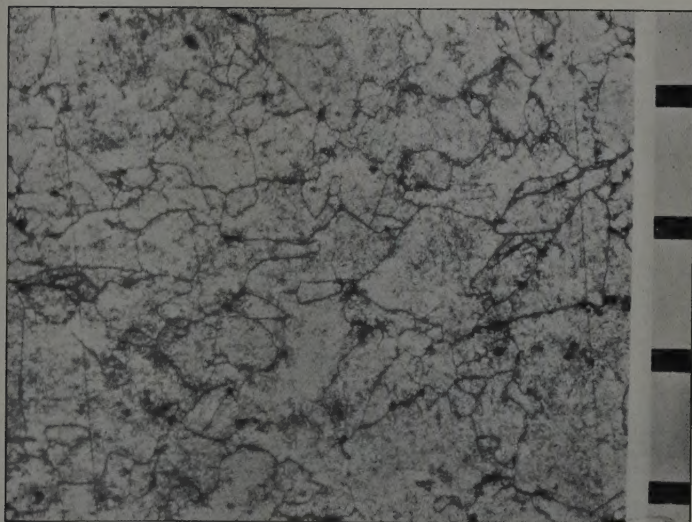
Chill-cast copper rod.

FIG. 2.



Filed particles

FIG. 4.



Nickel.

[The scale divisions represent 0.1 mm.]

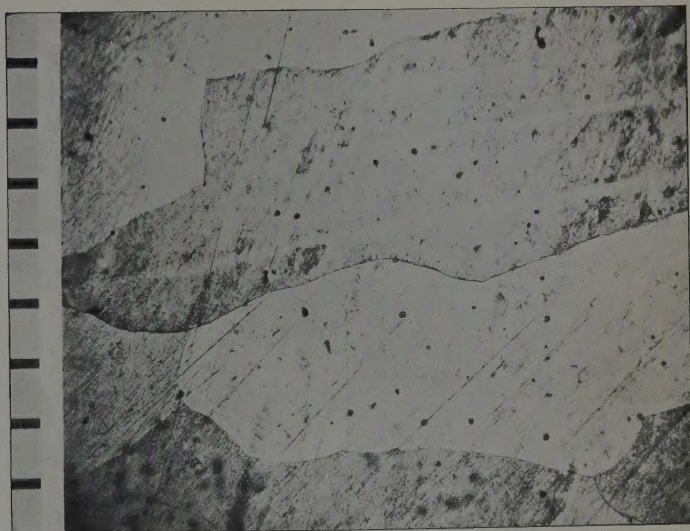
FIG. 3.



Hard-drawn copper wire.

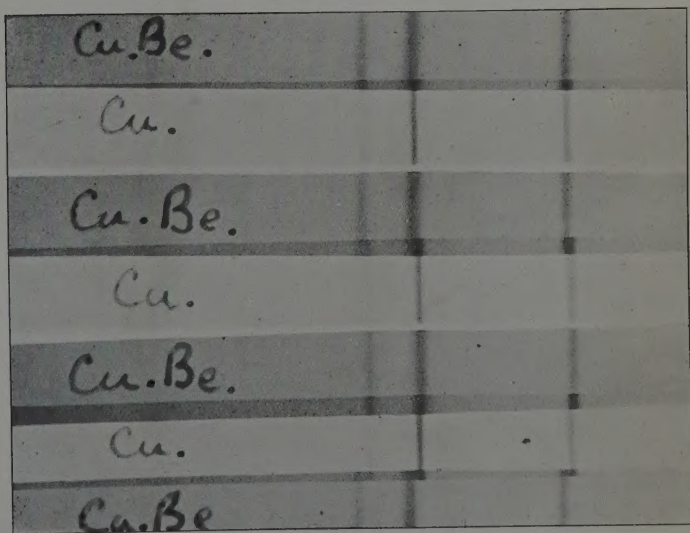


FIG. 1.



Microphotograph of CuBe alloy. [Scale divisions represent 0.1 mm.]

FIG. 2.



X-ray photographs of Cu and CuBe.

